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PREFACE

The fifth volume of the *Annual Review of Physical Chemistry* retains the framework of basic topics used in the previous volumes. In addition, there are some new topics and some revisions in the method of handling some of the older ones. A review of the subject of Cryogenics is presented for the first time. Nuclear and paramagnetic resonance has been separated from the review of microwaves in order to give a more complete coverage of these fields in which there is a great active interest at present. The review of polarography which appeared in some of the earlier volumes has been replaced in the current one by the broader topic of electrode processes. Another change has been the division of the review on chemical kinetics into two parts, one on reactions in solution and the other on those in the gas phase. Furthermore, since the major interest of those working in the field of photochemistry is the solution of problems in reaction kinetics, the review of photochemistry has been dropped and the authors of the reviews on kinetics have been asked to cover the photochemical papers. In the event that this procedure does not give a satisfactory coverage, the review of photochemistry will be reinstated in later volumes. Finally, it should be pointed out that a review of colloid chemistry appears again after a lapse of two years.

The Editorial Committee is continually seeking ways to extend and improve the coverage of the field of physical chemistry in these volumes. Any suggestions for new topics, or for the division or regrouping of the topics now covered, will be given careful consideration. The only limitation imposed is that such topics shall be suitable for at least a periodic review, if not an annual one.

Once more we have the pleasure of giving public expression of our thanks to the authors who have contributed to this volume. It is necessary to have the co-operation of outstanding scientists in order to obtain a satisfactory review of the tremendous number of papers on physical chemistry which appear each year. We believe that these volumes will be a great help to the physical chemists as long as we receive such co-operation.

B.L.C. W.F.L.
G.E.K. J.W.W.
J.G.K. R.E.P.
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THERMOCHEMISTRY AND THE THERMODYNAMIC PROPERTIES OF SUBSTANCES[1]

By L. E. Steiner

Department of Chemistry, Oberlin College, Oberlin, Ohio

Interest in thermodynamics in the past year has ranged from general theory and theory of specific systems to the securing of experimental data. Many of the data are now presented in tables of functions for substances in their standard states. The tables are extremely useful and we are grateful for all new data that help extend them. But, in practical problems we rarely meet pure substances in their standard states. To determine the values of the thermodynamic functions in real environments we need additional PVT data on pure substances and data on solutions, surface phenomena, and the like. However, limitations of space restrict our consideration of solutions, heterogeneous equilibria, electrode processes, and surface phenomena, which are topics covered in other parts of this volume. Limitations of time restrict the survey to papers which were available to the reviewer at the end of the current year.

Reviews of data.—Tables of best and internally self-consistent values of physical and thermodynamic properties of hydrocarbons prepared by Rossini and his co-workers (1) as part of the American Petroleum Institute Research Project 44 have been available in loose-leaf form and as National Bureau of Standards Circular Number C461. The tabulations are now published in a volume of 1050 pages under the title "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds." Critical reviews on special topics and with extensive bibliographies have appeared during the year. Long (2) discusses the heats of formation of simple inorganic compounds and their relation to the periodic table, crystal energies, bond energies, and to other physical properties. Brewer (3) reviews the thermodynamic properties of oxides and their vaporization processes. Baughan (4) the thermochemistry of the elements of Groups IV and IVb, and Kobe & Lynn (5) review the critical properties of elements and compounds.

General theory.—The theory and application of irreversible thermodynamics are discussed in a number of papers. Stueckelberg & Wanders (6) extend thermodynamics to the space-time of general relativity, and Kluitenberg, de Groot & Mazur (7) develop the relativistic thermodynamics of irreversible processes. Others discussing the theory of irreversible thermodynamics are Reik (8), Glandsdorff (9), Prigogine & Mazur (10), Gilbert (11), Popoff (12), and Hall (13). Among the theoretical questions not fully resolved is the applicability of such concepts as "minimum production of

[1] The survey of the literature pertaining to this review was completed in December, 1953.

energy" and "thermodynamic state of substances" to systems far from equilibrium. In view of the general reliance on the Onsager reciprocity relations, the conclusions of Thomsen (14) are interesting. He has examined the logical relations among five principles of statistical mechanics and thermodynamics: (*a*) detailed balance, (*b*) microscopic reversibility, (*c*) ergodic hypothesis, (*d*) the second law, and (*e*) restriction on the transition probabilities (λ hypothesis). He finds that the last three are equivalent, and that (*a*) and (*c*) together are equivalent to (*b*). Therefore, microscopic irreversibility is stronger than the second law. Yomoso (15) considers the problem of the creation of order in photosynthesis and the thermodynamic approach to biological phenomena, and concludes that the entropy change of the reaction system may be negative. Among those discussing the thermodynamics of irreversible electrochemical phenomena are Van Rysselberghe (16); Prigogine, Mazur & DeFay (17); de Groot, Mazur & Tolhoek (18); and Kemp (19). The last two disagree on the equation for the entropy change. There are also some theoretical discussions of electrochemical processes based on classical thermodynamics. Barieau (20) and Li (21) have disagreed on the correct application of the Gibbs-Helmholtz equation to reversible cells in which the composition of some phases vary with temperature. Stout (22) shows that the methods of the two are equivalent.

Data of State For Gases, Liquids, and Solids

Gases.—Pressure-volume-temperature relations of gases are commonly reported in terms of virial equations of state, with accompanying equations for the variation of the virial coefficients with temperature, or in terms of compressibility factors. This section covers gas phases only. Systems involving equilibrium between gas and liquid or solid phases will be discussed in later sections.

New *PVT* data have appeared on argon between 0° to 600° C. and 10 to 80 atm. [Whalley, Lupien & Schneider (23)]; on propene between 25° to 150°C. and up to 2500 atm. [Michels *et al.* (24)]; on ethane between 30° to 150°C. and 0.5 to 2.0 atm. [Hamann & McManamey (25)]; and *o*-, *m*-, and *p*-methyl styrenes at 100 and 760 mm. [Clements, Wise & Johnsen (26)]. Maslan & Littman (27) derive generalized compressibility charts for H, He, Ne, and A. For the *PV* relations of hydrogen and deuterium at 64.5° and 78.9°K between 150 and 1250 atm. David & Hamann (28) find a marked quantal inflation of the pressure, in agreement with the quantized Lennard-Jones and Devonshire theory of gases. Helium also shows quantal effects but the classical theory is fairly good for argon and nitrogen. According to Ter Haar (29), introduction of the Lennard-Jones potential energy function implies *a priori* assumption of corresponding states for gases.

Among those discussing the theory of the virial development of an equation of state for monatomic gases are Riddel & Uhlenbeck (30), Kilpatrick (31), and Woolley (32). Woolley derives the equation of state from the equilibrium constants for the formation of molecular clusters in an ideal gas

in which the effective number of molecules is identified with the total number of clusters of all kinds. [See also Duclaux (33).] Kilpatrick (34) points out that the number of clusters of a given size for a real gas frequently turns out to be negative, yet a model based on the cluster idea leads to the correct virial expression; the imaginary parts (negative number of clusters) cancel out.

Mizushima, Ono & Ono (35) calculated the second virial coefficient for hydrogen at low temperatures, and Green (36) calculated that for helium. [The values below 2°K are criticized by Ter Haar (37).] Second virial coefficients as functions of temperature are reported for SiF_4, SF_6, C_2N_2, and propadiene [Hamann, McManamey & Pearse (38), who conclude that the 12:6 potential is not a good description of the complex interactions of hydrocarbon molecules]; benzene (39); 2-methyl-2-propanethiol (40); and 3-methylthiophene (41). The second virial coefficients of polar vapors and of their binary vapor mixtures show systematic deviations from the principle of corresponding states [Lambert (42)]. The compressibilities of air up to 2200 atm. [Michels, Wassenaar & van Seventer (43)] and of nitrogen, and for nitrogen and ethylene mixtures up to 660 atm. [Hagenbach & Comings (44)] are reported. Michels & Boerboom (45) measured the volume change of mixing of two different gases for H, He, N, A, CO_2, CH_3F, C_2H_4, and propylene. According to Gorski & Miller (46) the interaction coefficients for the mixtures CO_2-N_2 and O_2-N_2, calculated from the individual second virial coefficients, agree satisfactorily with theoretical value of the Lennard-Jones and Cook force constants, but those for the mixture CO_2-O_2 do not.

Equations of state.—Several new equations of state have been proposed. One by Duclaux (47) is

$$P(V - b)/RT = A + B \log (V - b)$$

where A and B are functions of temperature only. For saturated vapors and for the determination of critical constants Kordes (48) proposes the equation, $P[V_g + V_{liq.} + \text{const.}] = RT$, where the constant is $R\theta/\pi - 2\phi$ (θ is the reduced temperature, π the reduced presure and ϕ the molar critical volume). According to Broch (49) the fugacity coefficient χ for saturated vapors of water and ammonia is represented by the equation, $K \log (1/\chi) = P^n$. Van Dranen (50) has proposed that at the critical point the average kinetic and potential energies are equal. The usual equations of state are not consistent with the hypothesis.

Critical phenomena.—The new data on phenomena in the critical region confirm those reported last year. In a long, thin tube of xenon mounted vertically at temperatures near the critical temperature, different horizontal sections of the tube have different isotherms according to Schneider & Habgood (51). This behavior is consistent with the classical idea of a unique critical point if the added effects of a gravitational field are taken into account. The coexistence curves of ethane, ethylene, and xenon at the critical temperatures have flat sections which decrease with height of system and with stirring. Whiteway & Mason (52) conclude that the major part of the

flat-top effect can be attributed to the effects of gravitational compression. Critical pressures and temperatures are correlated by Varshni (53) for normal paraffins, and by Organick (54) for complex hydrocarbon mixtures. Critical constants reported are: uranium hexafluoride (55, 56); *o*-, *m*-, and *p*-methyl styrenes (26); nitrous oxide, carbon dioxide, and mixtures of the two [with orthoboric densities, Cook (57)]. Other critical data may be found among the papers on phase relations.

Vapor pressure.—Two new vapor pressure equations are proposed to apply to real gases. Gottschal & Korvezee (58) show that for a gas whose equation is $PV=RT+BP$, three temperature dependent terms must be added to the mean heat of evaporation, L_v, and consequently to log P to give log $P_{corr.}=-A/T+b$. Frost & Kalkwarf (59), on the basis of a linear variation of L_v with T and the van der Waals a/V^2 as the gas nonideality term, derive a semiempirical equation with four constants. The third constant arises from the linear variation of L_v with T; The fourth arises from the a/V^2 term and equals $a/2.303R^2$. Its value can be calculated; the other three constants are evaluated empirically. The equation represents experimental vapor pressures from the triple point to the critical point with an average deviation of 0.3 per cent. Thomas (60) derives a general equation for correlating vapor pressures, temperature, and entropy of evaporation for any two nonassociated liquids. Duclaux (61) presents a new equation for treating the vapor pressure data for water and applies it in the range 0° to 100°C.

Many vapor pressure data (with equations) have been reported. Latent heats of evaporation or sublimation are usually derived from the data and sometimes the latent heats of melting. The corresponding changes in entropy may also be reported. Evans (62) reviews the free energy of evaporation of the metallic elements from 0° to 2000°C. Vapor pressures are reported for the elements: carbon (63); N_2 (64); F_2 (65); liquid and solid Cu (66); Ga (67); Ag (68); Hg (69); Sn (70); Cu and Ti (71). For inorganic compounds data are: HF (72); N_2O (57) (substantially lower than I.C.T. values); BI_3 and SiI_4 (73); diborane (74, 75); SO_2F_2 (76); SeF_4 (77); liquid $TiCl_4$ (78); liquid and solid UF_6 (55, 56); liquid and solid Tc_2O_7 (79); KCl (80, 81); KCl, RbCl, CsCl (82). The vapor pressures of solids at high temperatures are frequently determined by the Knudsen method: by the rate of effusion through an orifice in the crucible. Rossman & Yarwood (83) discuss the accuracy of the method, and Whitman (84) criticizes their assumptions.

Vapor pressures of organic compounds are reported as follows: hafnium alkoxides (85); esters of arsenious acid (86); Bu_3B, Bu_2BBr, and Bu_2BCl (87); solid and liquid hexamethyl cyclotrisiloxane and liquid octamethyl cyclotetrasiloxane (88); trimethylsilanol and triethylsilanol (89); tetrafluoroethylene (90); the deuterio-methanes (91); propene (24); cyclobutane (92); thiacyclobutane (93); *n*-nonane (94); pyridine and 5 of its homologues (95); *o*-, *m*-, and *p*-methyl styrene (26); naphthalene, anthracene, phenanthrene, fluorene, biphenyl, and pyrene (96); anthracene and 9,10-diphenylanthracene (97); 4 substituted benzotrifluorides (98); ethyl esters of 10

acetylated amino acids (99); 2-methyl-2-propanethiol (40); bis(hydroxymethyl) peroxide (100); cyclonite and pentaerythritol tetranitrate (101); oxamide, oxamic acid, and rubeanic acid (102); α- and β-anhydrous oxalic acid and tetragonal pentaerythritol (103) 2-thenoic acid, 2-furoic acid, and 2-pyrrolecarboxylic acid (104).

Phase transitions.—Melting and boiling points are often determined in connection with other measurements, such as vapor pressures and heat capacities. A number of values for the transitions and for other physical properties will be found in the papers cited in these connections.

Dugdale & Simon (105) have determined the melting curve of solid helium between 4° and 26°K and pressures up to 3000 atm. The melting temperature at 26°, which is five times the critical temperature, is relatively greater than that obtained for any other substance. At the highest pressure solid helium is compressed to less than half its volume under equilibrium conditions at absolute zero. The Lindemann melting formula fits the data. The melting curve shows no sign of approach to a solid-fluid critical point. The experiments indicate that it is impossible to melt a substance by adiabatic, reversible compression since such compression would lead further into the range of stability of the solid. These results have astrophysical and geophysical applications. Simon (106) has made estimates of the melting of iron at high pressures and proposes the equation, $P_{atm.} = 150{,}000[(T/1800)^4 - 1]$ which reduces to $P_{atm.} = 1.4[T/100]^4$ at very high pressures. These values are of geological interest. The limits of the graphite-diamond equilibrium were tested by Slawson (107) through the reaction, $HgC_2 = Hg + 2C$, which produced pressures as high as 35,000 kg./sq. mm. The carbon produced was identified as graphite. Jamieson (108) reports equilibrium pressures for the calcite-aragonite transition.

The heat capacities curves of some solids show peaks not associated with changes in density or in crystal system. These transitions, called "second-order" or λ transitions, are associated with "order-disorder" phenomena. Weir (109) through PVT measurements on rubber sulfur vulcanates has studied a λ transition for this system of glass type. He found no measurable change in transition temperature with increasing pressure and no noticeable discontinuity in compressibility at the transition. He reports "no ΔV_T and no L though C_p changes markedly." Hoffman & Decker (110) found reversible λ transitions for solid n-bromides and paraffins of high chain lengths in addition to first-order transitions. Johnston & Hallett (111) report a value of $\Delta S = 1.22$ cal./degree-mole for the second-order transition of sodium borohydride at 189.9°K. Stockmayer & Stephenson (112) associate this order-disorder transition with the orientation of the BH_4^- ions, corresponding to the behavior of NH_4^+ ions in crystals of ammonium halides. Stephenson, Corbella & Russel (113) find that the known transition in KH_2PO_4 or $NH_4H_2PO_4$, associated with orientation of hydrogen bonds in the tetragonal lattice, occurs when Rb or Cs are substituted for K or NH_4, AsO_4 for PO_4, and D for H, although the last substitution causes marked increase in transition temperatures. Other

second-order transitions reported are: $(NH_4)_2O$ (114); ammonium chromium alum (115); polyhexamethylene adipamide and sebacamide (116); butadiene-styrene copolymers (two glass transitions) (117). Additional transitions shown by anomalous high heat capacity are: cyclobutane (92); CuO (118); Fe_2TiO_4 (with two peaks) (119); and NaO_2 and KO_2 (120) (each with two peaks). Seyer (121) finds evidence for a λ region for liquid *cis*-decahydronaphthalene suggested by the heat capacity data of Parks & Hatton (122).

Compressibility and phase equilibria.—For dilute mixtures of water vapor with hydrogen, helium, and argon Flood (123) finds that the thermodynamic potentials do not differ from those of the pure components, at equal volume concentration, by more than 0.3 per cent. Since the Gibbs-Dalton law applies, Dalton's law must apply. On the other hand, Webster (124) finds that the theoretical increase of vapor pressure under the pressure of an inert gas, as calculated by the Poynting thermodynamic relation, is usually much less than the actual vapor pressure elevation. The difference is attributed to a solubility effect. Some vapor-liquid equilibria reported are: Otsuki & Williams (125) ethyl alcohol-water at pressures up to 20 atm.; Furukawa & McCoskey (126) the condensation line for air; Llewellyn (55) vapor and liquid densities of uranium hexafluoride; Carmichael, Sage & Lacey (94) *n*-nonane up to 238°C. and 665 atm.

Among the binary liquid-vapor systems measured under wide ranges of temperature and pressures are: Selleck, Reamer & Sage (127) NO-NO_2; Cines *et al.* (128) and Bloomer & Parent (129) CH_4-N_2; Sage and co-workers (130) propane-H_2; pentane-H_2S (131), decane-H_2S (132); Kay and co-workers (133) CO_2-H_2S, ethane-H_2S (134), propane-H_2S (135); Kobayashi & Katz (136) propane-H_2O.

Helium

The peculiar behavior of liquid helium (helium II) below its transition temperature (λ point) at 2.19°K. is still not clarified. None of the models suggested explain all the available data on helium II and on He^3-He^4 mixtures in the helium II range. A number of theoretical papers have appeared but we shall consider here only the papers presenting experimental data on helium. Two reviews on special topics—one by Pellam (137) on second sound (heat pulses) in liquid helium II and another by Long & Meyer (138) on the unsaturated helium film—summarize the work in these fields.

According to Reekie, Hutchison & Beaumont (139, 140), liquid helium has a typical liquid-ring type of x-ray diffraction pattern with no outstanding difference in structure above and below the λ point. They suggest that a simple tetragonal lattice with axial ratio, $c/a=\sqrt{2}$, will approximately satisfy the distribution just below the λ point. If 8 of 12 nearest neighbors in a face-centered cubic lattice are removed, the result is a set of 100 planes more densely populated than any other planes. Such an ordered structure for the "superfluid component" would agree with $S=0$. Bombardment of the superfluid portion by normal atoms would lead to destruction of the order. Swen-

son (141) finds that the melting curve from 1.5 to 4°K. is in good agreement with the assumption that the λ transformation is of the second order. Measurements of "second sound" and of heat capacity and entropy are used by de Klerk, Hudson, & Pellam (142) to calculate the "normal fluid concentration" of helium II from 0.15°K. to the λ point. The velocity of ordinary sound, measured by Atkins & Stasior (143) between 1.2° and 4.2°K. at pressures up to 69 atm. yields curves which show no detectible discontinuity along the λ path. The vapor pressure data of Abraham, Osborne & Weinstock (144) on liquid He^3 are used by Ter Haar (145) to test their suggestion that liquid He^3 has a transition below 1°K. Ter Haar fits the data by two equations and concludes that such a transition exists unless the measurements are in error. Chen & London (146) fit the same data to a six-constant equation. The entropy curve derived from it goes smoothly to zero at 0°K. and lies very close to the theoretical curve for a Fermi-Dirac smoothed-potential liquid below 1°K. Weinstock, Abraham & Osborne (147) use melting-pressure data to show that calculations implying that nuclear spins of liquid He^3 are appreciably aligned above 0.5°K. are inconsistent with the assumption that the nuclear spins are randomly oriented in the solid. They present an equation for the entropy, including a nuclear spin term.

The fact that He^3 in helium II does not behave as a superfluid was utilized by Atkins *et al.* (148) to separate He^3 from He^4. With a super leak, they increased the He^3 concentration from 2 to 64 per cent in a single operation. On the basis of measurements of the wave velocity of second sound in He^3-He^4 mixtures, Weinstock (149) concludes that Pomeranchuk's theory (150) is incorrect, but King & Fairbank (151) find that the velocity passes through a maximum as the temperature of the mixtures approaches zero, in agreement with Pomeranchuk's theory. Keesom, Bijl & Monté (152) have prepared a log *T*-*S* chart for the entropy of helium for temperatures 1° to 500°K. and pressures up to 300 atm.

Latent Heats and Transition Temperatures

Many heats of vaporization and sublimation (and heats of melting derived from them) have been calculated from the vapor pressure data reported in an earlier section. From the variation of evaporation of carbon with temperature Chupka & Inghram (63) derive a value of 178.5 ± 10 kcal./mole for the heat of sublimation at 0°K. They report a C/C_2 ratio of 1.2 at 2300°K. Their results are of special interest since the value for the heat of sublimation for carbon is in dispute. Among the latent heat values measured calorimetrically in connection with low temperature, heat-capacity measurements and the corresponding transition temperatures are: Heats of melting: F_2 (65); HF (153); diborane (74); Hg (69); NH_4OH, $(NH_4)_2O$ (114); thiacyclobutane (93); 3-methylthiophene (41); 2-methyl-2-propanethiol (40); tetrafluoroethylene (90); cyclobutane (92); methyl nitrate (154); some C_7H_{14} alkylcyclopentanes (155). Some high temperatures heats of melting and melting temperatures are: MoO_3 at 1068.36°K. (156); Nb_2O_5 at 1785°K. (157) Wil-

hoit & Dole (116) have measured the heats of melting of some high polymels (nylons) and of 3 monomers.

Some calorimetric heats of vaporization are: F_2 (65); HF (153); diborane (74); thiacyclobutane (93); 3-methylthiopene (41); 2-methyl-2-propanethiol (40); tetrafluoroethylene (90); cyclobutane (92); chlorotrifluoroethylene (158); oxygen and nitrogen (126); mercury (159).

Data on Heat Capacity, Enthalpy, and Entropy

Most of the papers reporting low-temperature heat capacities also report values of S, $H-H_0$ or $(H-H_0)/T$, and $F-H_0$ or $(F-H_0)T$, usually in tabular form at regular temperature intervals. Since high-temperature measurements usually furnish values of enthalpy relative to that at 298.16°K., the values reported from them are $H-H_{298.16}$, C_p, and $S-S_{298.16}$, expressed in tabular form or in equations. The enthalpies and entropies for any phase transitions are also reported. If low-temperature data are available, the high-temperature data may be combined with them and the reference temperature becomes zero absolute.

Low-temperature data.—The low-temperature data, based on experimental heat capacities and usually tabulated from low temperature to 300°K., which have appeared during the year are: Hu, White & Johnston (65) F_2 to 85°K.; Hildenbrand & Giauque (114) NH_4OH and $(NH_4)_2O$; De Sorbo & Tyler, (160) graphite; De Sorbo (161) diamond, (162) selenium; Busey & Giauque (69) mercury; Kothen & Johnston (163) titanium; Smith, Oliver & Cobble (164) rhenium; Griffel & Skochdopole (165) thorium; Bauer & Johnston (166) red mercuric oxide; Hu & Johnston (118) cupric oxide; Todd (167) HfO_2 and $HfCl_2$; Westrum, Hatcher & Osborne (168) NpO_2; Osborne & Westrum (169) ThO_2; De Sorbo (170) Cr_3C_2; Hallett & Johnston (171) lithium borohydride; Cobble, Oliver & Smith (172) potassium perrhenate; Johnston, Hu & Horton (115) ammonium chromium alum; Scott *et al.* (93) thiacyclobutane, McCullough *et al.* (41) 3-methylthiophene, (40) 2-methyl-2-propanethiol.

Other low-temperature data on heat capacities and derived values of entropies and sometimes of enthalpy are: Todd (120) NaO_2, KO_2, Na_2O_2; Johnston and co-workers (74, 75) diborane; King & Todd (173) SnS and SnS_2, Todd & King (119) Fe_2TiO_4 and Fe_2TiO_5; Kelley *et al.* (174) some minerals of sodium-aluminum and potassium-aluminum silicate series. Hu & Johnston (153) find a difference of 17.5 cal./degree-mole between the calorimetric values for hydrogen fluoride and the value calculated from spectroscopic data. This difference is accounted for by the equilibrium mixture of monomer, dimer, and trimer, etc., in the gas phase. [See also Jarry & Davis (72).]

Values on organic compounds include: Furukawa, McCoskey & Reilly (90) tetrafluorethylene; Rathjens & Gwinn (92) cyclobutane; Gray & Smith (154) methyl nitrate; Gross, Oliver & Huffman (155) some C_7H_4 alkylcyclopentanes; Furukawa, McCoskey & King (117) some butadiene-styrene polymers.

High temperature data.—High-temperature enthalpy data with accompanying entropies and heat capacities are: Cosgrove & Snyder (156) MoO_3 to 1300°K., Orr (157) Ta_2O_2 to 1800°K. and Nb_2O_5 to 1810°K.; Orr (175) HfO_2 to 1800°K. and $HfCl_4$ to 485°K.; Coughlin & Orr (176) $SrTiO_3$, $SrTiO_4$, $BaTiO_3$, and $BaTiO_4$ to 1800°K.; Orr (177) Mg_2SiO_4 and Fe_2SiO_4 to 1800°K.; Copper (178) KBr to 720°K. and KI to 700°K. Drummond & Barrow (179) have calculated values of crystalline and gaseous enthalpies of beryllium oxide at 2300°K. and the heat of sublimation. Kelley *et al.* (174) report high-temperature increments to the low-temperature data for the enthalpy and entropy of several silicate minerals.

Thermodynamic functions from spectroscopic data.—The usual thermodynamic functions for the ideal gas, derived from spectroscopic data C_p°, S°, $H^\circ - H_0^\circ$ or $H^\circ - H_0^\circ/T$, and $-(F^\circ - H_0^\circ)/T$ usually to 1500°K., are reported by the following: For the halogenated methanes (39 compounds) Gelles & Pitzer (180) calculate values based on recently revised vibrational frequency assignments and recent constants. Spectroscopic data and frequency assignments, together with the calculated thermodynamic properties, are reported by McGee *et al.* (181) CF_3Br and CF_3I; Weber, Meister & Cleveland (182) CH_2BrCl; Bernstein, Zietlow & Cleveland (183) CCl_3F; Decker *et al.* (184) CBr_2F_2; Rathjens *et al.* (185) cyclobutane; Mann, Acquista & Plyler (186) chlorotrifluoroethylene; Pitzer & Hollenberg (187) methyl chloroform; McDowell (188) thionyl chloride; Hawkins & Wilson (189) SiH_2Cl_2; Lippincott & Tobin (190) lead tetramethyl, and germanium tetramethyl; Hrostowski & Pimental (191) three monomethyl cyclopentanes and nine dimethyl cyclopentanes (from the values for cyclopentane by the method of the methyl increment); Scott & Waddington (192) 2,2,3-trimethylbutane (with comparison of calculated and experimental entropies at several temperatures). Person & Pimental (193) have revised Pitzer's values for the *n*-paraffins from butane to eicosane (method of methyl increments for the compounds beyond heptane) and have compared the calculated and experimental values of C_p° and S° for hexane, heptane, and octane at 298.16°K. Luft (194) calculated the functions for FCN to 1000°K. and Griffel (195) those for potassium vapor to 3000°K. Sherman & Giauque (196) have recalculated the free energies and entropies of hydrogen, chlorine, and hydrogen chloride with the modern physical constants.

Heat capacity.—After discussing various heat capacity theories Kelly & MacDonald (197), conclude that in spite of its limitations the Debye theory for solids is the most useful representation for general analysis. Leibfried & Brenig (198), by approximating the spectrum of lattice vibrations in a solid by a combination of Debye and Einstein terms, are able to describe the anomalous heat capacities of the alkali metals quantitatively. Ito (199) discusses the heat capacity of solids in terms of an assembly of 3N one-dimensional oscillators. The theory yields a correct mean energy but an incorrect energy fluctutation. Stockmayer & Hecht (200) calculate the frequency spectrum and heat capacity of a simple model of a large crystal composed of

long, parallel polymer chains. The heat capacity is very unlike that of a cubic crystal but it can be represented by a simple two-parameter equation proposed by Tarasov (201). Data on the heat capacity of layer and chain types of solids at low temperatures are discussed in the following section.

Barrow (202) derives the heat capacity of vapors from the constants of the Frost (59) vapor pressure equation in which the third constant is related to the variation of L_v with temperature and the fourth constant is related to the gas imperfection of the vapor. If the difference in heat capacity of saturated vapor and liquid ($\Delta C_{\text{satn.}}$) is approximated by $\Delta C_{\text{satn.}} \doteq \Delta C_p = C_{p\text{(vapor)}} - C_{p\text{ (liq.)}}$, knowledge of the heat capacity of the liquid permits evaluation of that of the vapor. If corrections are made for the gas imperfection the value of C_p° for the gas can also be calculated. For a number of organic liquids Chow & Bright (203) present a method for predicting heat capacities from values of the structural parachor and the molar refraction. Kwang-Tzu (204) calculates C_p for gases as a function of temperature and pressure by use of the Joule-Thomson coefficient.

As part of the program of the U. S. Bureau of Standards in supplying standards to be used in precise calorimetry Ginnings & Furukawa (205) have redetermined the heat capacities of *n*-heptane and aluminum oxide (corundum). Tables of smoothed values of $C_{\text{satd.}}$ and $H - H_0$ for these substances and for benzoic acid, diphenyl ether, and water are given. Direct measurements of C_v; and C_p at 1 atm., are reported on *n*-pentane and alcohol [Bryant & Jones (206)]. For alcohol C_v was measured at pressures up to 750 atm. Fine (207) has calculated the value of $C_p - C_v$ for silicon and germanium from the coefficient of linear expansion, the isothermal compressibility and the atomic volume and compared the results with those calculated with the Nernst-Lindemann formula. The latter gave results consistently too high; there was actually less error if C_p and C_v were assumed to be equal. Staveley, Hart & Tupman (208) report values for C_p, the coefficient of expansion, and the adiabatic compressibility for C_6H_6, CCl_4, ethylenedichloride, HOAc, $CHCl_3$, acetone, and CS_2 and for some binary mixtures of these and derive C_v values from the data. Lacam & Noury (209) used the velocity of ultrasonic waves to determine the ratio, C_p/C_v, for nitrogen and argon under pressure; argon was measured at pressures up to 900 atm. Woolley (210), using the resonance method and considering the mass effect of the gas, obtained C_p/C_v values for N_2, A, CO_2, N_2O and SO_2 which agreed with values obtained from spectroscopic and PVT data.

The change of heat capacity with pressure at low pressures is reported for perfluorocyclobutane [Masi (211)] and hexafluoroethane [Wicklund, Flieger & Masi (212)]. Other C_p values are: Sinke & De Vries (213) vapors of 9 aliphatic alcohols (methyl to amyl); Michels *et al.* (24) propene, up to high pressures; Seyer (121) *cis*- and *trans*-decahydronaphthalene; Wilhoit & Dole (116) polyhexamethylene adipamide and sebacamide; Pochapsky (214) AgBr. For diamonds of Types I and II of gem quality Berman & Poulter

(215) find heat capacities which agree with De Sorbo's values. The values for opaque diamonds are higher, agreeing with Pitzer's values.

Heat capacities at low temperatures.—For many solids the Debye formula, derived for an isotropic solid, predicts successfully the variation of low-temperature heat capacity with the third power of the absolute temperature. In 1945, Tarasov (216) applied the concept of an elastic continuum to solids with large chains and nets and obtained expressions for the heat capacity of linear and two-dimensional molecules. At low temperatures they indicate, respectively, a T and a T^2 variation of C_v with temperature, but the expressions cannot be used at very low temperatures where the Debye method is not applicable.

Below 4°K. Keesom & Pearlman (217) find that the lattice contributions follow the T^3 law for a single crystal of potassium chloride and for polycrystalline, single crystal, and crushed germanium (218). Graphite follows a T^2 law between 13° and 54°K. [De Sorbo & Tyler (160)]. According to Krumhansl & Brooks (219) this behavior as a consequence of the elastic anisotropy of graphite and is an intrinsic property rather than an effect of particle size as suggested by Gurney. The theory of Krumhansl and Brooks predicts a T^3 dependence for graphite at very low temperatures whereas the Gurney theory predicts a T^2 dependence down to absolute zero. De Sorbo and Tyler suggest that data on graphite in the helium temperature range are needed to decide this point. Boron nitride has a T^2 dependence very exactly up to 60°K. [Dworkin, Sasmor & Van Artsdalen (220)], and the data of Adams *et al.* (221) on gallium between 15° and 34°K. show a T^2 dependence [De Sorbo (222)]. At the lowest temperatures selenium and tellurium have a T^3 dependence but selenium agrees with a one-dimensional continuum model down to 37°K. De Sorbo (162, 223) describes the variations in terms of an anisotropic continuum with interactions between the atom chains. Tungsten and molybdenum between 1° and 77°K. have a T^3 lattice contribution [Horowitz & Daunt (224)], and normal niobium follows the T^3 dependence below 5°K. [Brown, Zemansky & Boorse (225)]. Hill & Smith (226) obtain the anomalous contribution of the ferrous ion to the heat capacity from the difference between the heat capacities of ferrous ammonium sulfate and zinc ammonium sulfate. Osborne & Westrum (168, 169) use the C_p and S values for ThO_2 to evaluate the magnetic contribution of UO_2 and NpO_2; and Roberts, Sartain & Borie (227) evaluate the nuclear and electronic contributions to the heat capacity of neodymium ethyl sulfate (3 Nd isotopes).

Heats and Free Energies of Reaction

Heats of combustion and formation.—Heats of formation are frequently derived from calorimetric heats of combustion but they may also be derived from other series of reactions. Hence, only some of the reported heats of formation will be covered in this section. Heats of combustion of elements, which yield heats of formation of the oxides directly, are reported by Cos-

grove & Snyder (228) beryllium; Huber & Holley (229) cerium (the values differ by 7 to 12 per cent from previous values) and (230) lanthanum; Humphrey (231) hafnium and HfN; Boyd, Cobble & Smith (232), rhenium, and ReO_3, to form Re_2O_7; Humphrey & O'Brien (233) tin, and SnO, to form SnO_2.

Coops and his co-workers have measured the heats of combustion of a number of hydrocarbons: (234) thirteen *p*- and *o*-tolylethenes and phenylbutadienes, (235) four diarylethynes, (236) eight phenylethanes, and (237) nine *p*- and *o*-tolylethanes and phenylbutanes. Smith *et al.* (238) report the heats of combustion of 130 organic chloro compounds by the "quartz wool" method. Other heats of combustion and formation are: Lippincott & Tobin (190) lead tetraethyl and tin tetraethyl; Scott *et al.* (93), thiacyclobutane; McCullough *et al.* (41) 3-methylthiophene, (40) 2-methyl-2-propanethiol; Fagley, Klein & Albrecht (239) diazoaminobenzene, benzotriazole, 2-triazoethanol; and Thompson (240) some linear polydimethylsiloxanes. Ito (241) shows that for hydrocarbon molecules a summation of the interatomic bond energies does not always give the correct heat of formation. When the interactions between nonbonded atoms are taken into account the observed heats of formations and their differences in homologous series can be explained. Franklin (242) proposes a method for calculating the heats of formation of gaseous free radicals and of carbonium ions.

Other heats of reaction.—Heats of formation calculated from measured heats of hydrolysis are: Skinner & Smith (243) BCl_3; Charnley & Skinner (244) PCl_3, PBr_3, $POCl_3$, $POBr_3$; Charnley, Mortimer & Skinner (86), the methyl, ethyl, and propyl esters of arsenious acid. Other heats of reactions are: Mortimer & Skinner (245) phenylarsine with iodine (and the heat of solution of HI in CCl_4); Hildenbrand & Giauque (114) $(NH_4)_2O(liq) = NH_4OH(liq) + NH_3(g)$; Sturtevant (246), hydrolysis of amide and peptide bonds; Setton (247) $n\text{Cs} + n\text{CO} = (\text{CsCO})_n$; Coulter (248) reaction of Li, Na, K, Cs, Ca, Sr, and Ba with NH_4Br, NH_4Cl, and NH_4I in liquid ammonia, and solution of the metals in liquid ammonia; Latimer & Jolly (249) heats of solution of NaF in water and in aqueous solutions of $Al(NO_3)_3$; Cobble, Smith & Boyd (250) formation of $HTcO_4$ aq. from Tc, O_2, and H_2O, and solution of $HTcO_4$ and Tc_2O_7; Katzin & Ferraro (251) solution of $CoCl_2$ and four hydrates in water and in seven organic solvents; Andrianov & Pavlov (252) hydrolysis of $SiCl_4$, $MeSiCl_3$, Me_2SiCl_2, Me_3SiCl, $EtSiCl_3$, and $PhSiCl_3$; Kury, Zielen & Latimer (253) neutralization of aqueous H_2S (heat, free energy, and entropy of formation of HS^- and S^{--} are calculated); Jenkins & Style (100) solution of $(CH_2OH)_2O_2$ in water (heat of formation calculated); Coleman & Harward (254) neutralization of acid clays and cation-exchange resins; Mel, Jolly & Latimer (255) solution of $KBrO_3$ and reduction of BrO_3^- by Br^- and I^- (heat and free energy of formation of BrO_3^- are calculated); Hepler, Jolly & Latimer (256) solution of NaF in water and in $HClO_4$ solution (heat and entropy of ionization of HF, and entropy of HF_2^- ion are calculated); Gregory & Burton (257) solution of chromium II and III chlorides and iodides (heats of

formation of iodides calculated); Eyring & Westrum (258) solution of Th_2S_3 in acid (heat of formation calculated).

Some heats of mixing determined calorimetrically are: Yatsimerskiĭ & Grafova (259) copper-ammonia complexes in aqueous ammonia solutions; Lange & Möhring (260) alcohols in water and in octamethyltetrasiloxane; Copp & Everett (261) $EtNH_2$ and Et_2NH in water and EtOH; Dunlap (262) fluorocarbons and hydrocarbons; Korvezee, Ruiter & Stuyts (263) benzene and ethylene dichloride; Meares (264) aromatic hydrocarbons and phthalates. Tager & Dombek (265) measured the heat of solution of polystyrene in benzene.

Equilibrium measurements.—Equilibrium measurements yield equilibrium constants and standard free energy of reaction directly and these, combined with thermal values, yield heats and entropies of reaction. Or equilibria measured over a temperature range yield values for K, ΔF, ΔH, and ΔS. Such functions are reported from the following: Strohmeier & Briegleb (266, 267) gaseous association of hydrogen fluoride; Bauer, Shepp & McCoy (268) dissociation of diborane; Gilles & Margrave (269) dissociation equilibrium for F_2; Ditmars & Johnston (270) dissociation of Li(OH); Allen & Scaife (271) dissociation of nickel oxalate dihydrate; Schäfer & Oehler (272) $2FeCl_3(s) = 2FeCl_2(s) + Cl_2(g)$; Guérin & Boulitrop (273) $2As_2O_5 = As_2O_6(g) + 2O_2(g)$; Bennett *et al.* (274) $NH_2CONH_4(s) = 2NH_3(g) + CO_2(g)$; and Wilkins & Grant (275) dissociation of $SiF_4 \cdot NMe_3$. Koch & Cummingham (276) $SmCl_3(s) + H_2O(g) = SmOCl(s) + 2HCl(g)$, $GdCl_3(s) + H_2O(g)$; Gokcen (277) $\frac{1}{2}MoO_2(s) + H_2(g) = \frac{1}{2}Mo(s) + H_2O(g)$; Busey & Giauque (278) $NiCl_2(s) + H_2(g) = Ni(s) + 2HCl(g)$; Brooks (279) $2Cu(s) + H_2S(g) = Cu_2S(\gamma) + H_2(g)$; Bethune & Pidgeon (280) $ZnS(s) + Fe(s) = FeS(s) + Zn(g)$, $ZnS(s) + 2Cu(s) = Cu_2S(s) + Zn(g)$; Small (281) polymerization equilibrium of methylmethacrylate (measured by the vapor pressure of the monomer over the solution). Broser & Lautsch (282) formation of the clathrate compound between β-dextrin and crystal violet; Gray & Smith (154) $HNO_3 + CH_3OH = CH_3NO_3 + HOH$; Caldin & Long (283) $OH^- + EtOH = OEt^- + H_2O$; Lane, Linnett & Oswin (284) reaction of ethylene with HCl and HBr.

A number of equilibria of ions with complexing agents have been measured, usually at more than one temperature. The cations and complexing agents studied are: Latimer & Jolly (249) Al III with F^-; Spike & Parry (285) Cd II with NH_3, CH_3NH_2, and ethylenediamine, (286) Zn II and Cu II with NH_3 and ethylenediamine; Vanderzee & Dawson (287) Cd II with Cl^-; Warner & Weber (288) Cu II and Fe III with citrate; Lister (289) Cu III with tellurate and periodate. Irving & Williams (290) review the stability of metal complexes (first transition series) and give an extensive table of equilibrium constants. Evans & Nancollas (291) studied spectrophotometrically the association of $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ with Cl^-, Br^-, I^- and N_3^- ions.

Electromotive force measurements.—Equilibrium studies of the concentrations of the elements in their different oxidation states, combined with elec-

tromotive force measurements, may be used to determine the relative free energies of the states, the oxidation-reduction potentials, and the potential diagram for the elements. Such functions, and sometimes other thermodynamic functions, are derived from the following: Connick & McVey (292) report on the effect of α-particles on the disproportionation of Pu IV to Pu III and Pu VI (and its dependence on H^+ concentration) and Rabideau (293) reports emf. measurements on this system. Other systems studied are: Magnusson & Huizenga (294) Np IV-Np V in perchloric acid solution; Cobble, Smith & Boyd (232, 250) Tc IV-Tc VII (with the potential diagram of technitium); Waterbury & Martin (295) the Mn II, III, IV equilibrium in iodic acid; Hepler, Hugus & Latimer (296) the stabilities of In I, In II and In III; and Saltman & Nachtrieb (297) Ga-Ga III. From emf. studies Suzuki determines the heat and free energy of formation of Tl_2CrO_4 (298) and CuN_3 (299). Redox potentials of cobalt and iron carbonyls are reported by Hieber & Hübel (300). Wagner (301) reports on the Ag/S ratio in silver sulfide and on its variation in the presence of solid silver and liquid sulfur. He has also calculated the dependence on acid concentration of the potential of the saturated Weston cell (302). He recommends a modified cell to eliminate the dependence. Lietzke & Staughton (303) have investigated silver-silver sulfate and mercury-mercurous sulfate electrodes up to 250°C., and Pouradier & Chateau (304) the influence of temperature on the normal calomel electrode between 5° and 70°C. For the Fe-Fe II electrode Patrick & Thompson (305) find a new value of $E^\circ = 0.409$ *v*, and for the Hg-$(Hg)_2^{++}$ electrode Bonner & Unietis (306) find $E^\circ = -0.7961$ *v*.

Other equilibrium data.—Other equilibrium measurements, usually covering a range of temperature, are: Copeland, Silverman & Benson (307) vapor-liquid equilibrium for the system NaCl-H_2O at supercritical temperatures and pressures (they find a partial molal volume of NaCl in steam of the order of two liters, the largest ever reported); Diepen & Scheffer (308) solubility of naphthalene in supercritical ethylene; Spicer & Banick (309) solubility of In in Hg; Keck & Broder (310) solubility of Si and Ge in liquid gallium and indium. Thurmond (311) reports solubility equilibria for Ge and Si in the elements of Periodic Groups III, IV, and V. Bell & George (312) measured the solubility of thallium and calcium iodates in various salts (0° to 40°C.) to obtain dissociation constants of various thallous compounds. Doucet *et al.* (313) report on the solubility of electrolytes in molten silver nitrate, and (314) of $AgNO_3$ in KNO_3 Good *et al.* (315) measure the solubility of *p*-terphenyl in biphenyl and *o*- and *m*-terphenyls and Mod, Skau & Planck (316) the solubilities of α- and β-elestearic acids with each other and with acetamide. De Vries & Vanderkool (317) report freezing points and vapor pressures for the systems, CO_2-CH_2BrCl, CO_2-CBr_2F_2, and CO_2-$CBrF_3$. Rutledge, Jarry & Davis (318) report the freezing point diagram and liquid-liquid solubilities for UF_6-HF. Vapor pressures of metals over alloys are reported by Scatchard & Westlund (319) Zn over Zn-Ag; McCabe, Schadel & Birchenall (320) Ag over Ag-Au; and Vetter & Kubaschewski (321) Mg

over Mg-Sb and Mg-Bi. Thermodynamic properties are derived by Andon, Cox & Herington (322) from the vapor equilibria of some pyridine bases in water, by Doty & Myers (323) for the association of insulin molecules, by Allen & Caldin (324) for the dimerization of some carboxylic acids in benzene (from boiling points) and by Yamakita & Aida (325) from the distribution of palmitic, myristic, and lauric acids (monomer-dimer equilibrium). Sauerbrunn & Sandell (326) obtain ionization constants of osmic VIII acid from distribution equilibria.

Miscellaneous Topics

New apparatus and methods.—Among the new or modified apparatuses described are: Rifkin, Kerr & Johnston (75) a special high pressure calorimeter; Westrum, Hatcher & Osborne (168) calorimeter for gram samples and a modified cryostat; Clarke, Johnston & De Sorbo (327) new melting point calorimeters; Calvert (328) microcalorimeter with four thermally sensitive elements for adsorption, Clement *et al.* (329) and Lacaze & Peretti (330) carbon thermometers for very low temperatures; Dauphinee, MacDonald & Pearson (331); a Cu-Cu(Sn) thermocouple for low temperatures; Pfister & Günthard (332) small precise Pt-resistance thermometers; Oliver & Grisard (333) metal ebulliometers for measuring the vapor pressures of corrosive liquids over the entire liquid range; Charnley, Isles & Townley (334) apparatus for measuring the isothermal Joule-Thomson coefficient.

Miscellaneous.—The Reichsanstalt value of the normal boiling point of oxygen is about 0.04°K. too high according to Aston & Moessen (335) who compared Pt-resistance and He thermometers. The temperatures and combustion products of a number of combustion gases are described by Smith *et al.* (336, 337). The temperature of the cyanogen-oxygen flame according to Conway, Wilson & Grosse (338) is the highest yet recorded (4640°K.). Bent (339) suggests a simplified algebraic method for obtaining thermodynamic formulas.

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HETEROGENEOUS EQUILIBRIA AND PHASE DIAGRAMS[1]

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Following the monumental work of Van't Hoff (1) and his co-workers in applying the suggestions of Roozeboom (2) to the problems connected with the study of the Stassfurt deposits in Germany many years ago, the principle of the phase rule of Gibbs soon became widely accepted as a useful tool of the physical chemist in many fields. Today its application and the techniques involved form a major branch of physical chemistry, and the literature on this subject becomes increasingly prolific year by year. Therefore, the task of a thorough review becomes enormous and, as a consequence, the author has attempted to touch only upon some of the highlights of the past year's work in the many fields involved.

Heterogeneous systems have been classified in numerous ways, but probably one of the best methods is that proposed by Bogue & Newkirk (3) the authors of last year's review on Heterogeneous Equilibria and Phase Diagrams in the *Annual Review of Physical Chemistry*. This method is based on chemical composition to provide the following broad categories: (*a*) aqueous salt systems, (*b*) organic systems, (*c*) anhydrous salt systems, (*d*) metallic systems and, (*e*) oxides and refractory systems. In general, both the temperature range of interest and the problems of technique involved increase in the order in which these categories are listed.

In addition to references to work on various equilibrium systems falling into one or other of the above classifications, a brief review of advances in graphical methods and experimental techniques is first discussed under a separate heading.

Graphical Methods and Experimental Techniques

Phase diagrams and other graphical methods of representing equilibrium data often present perplexing problems, particularly in the case of multicomponent systems. The classical method of Jänecke (4) for plotting aqueous systems of reciprocal salt-pairs was used extensively by Van't Hoff and his numerous co-workers. However, since this involves the principle of plotting the difference of two values against a third value to obtain a two-dimensional plot in place of a three-dimensional solid, the utility of the resulting diagram is seriously impaired. Quantitative solutions of problems such as those involving isothermal evaporation and polythermal fractional crystallization in the application of the data to process design, for example, cannot be ob-

[1] The survey of the literature pertaining to this review was concluded as of December 1, 1953.

tained from such diagrams by direct graphical methods. Tedious calculations based on the original numerical data are required. Therefore, in recent years the use of triangular co-ordinates and the projection of solid models onto plane surfaces have become popular expedients for the phase rule chemist. However, even these methods in many cases have been found to be either cumbersome or inadequate for the purposes desired. The need for still further improvement in plotting methods has frequently been made apparent. This situation has been alleviated, to some extent at least, by a graphical procedure recently developed by Suhr (5), while a similar method was reviewed by Jänecke (6) in a published address. Five component systems, for example, may be considered in four dimensions projected into three-dimensional space for plotting purposes. Projections of such a model, in turn, may be shown in two dimensions for convenience. Such methods may be applied in the case of all multicomponent systems and have been found quite useful for practical purposes.

Also during the past year numerous contributions of a minor nature in the field of general application of the phase rule were also noted. For example, Jacobs (7) discussed the theorem of Duhem in comparison with the phase rule of Gibbs and gave examples in which Duhem's theorem may be extended to open systems. The mathematical derivation of the phase rule was reviewed by Brunello (8), while an interpretation was presented by Hollingsworth (9). Complete mathematics for a previously published graphical procedure (10) were discussed by Huber (11). Zernike (12) wrote an article of more or less elementary nature on the use of binary space models using volume, composition, and temperature as variables. Knapp (13) reviewed the use of curves to compare the free energy relations and composition at constant temperature and pressure to determine the range of stability of a phase or combination of phases. Examples were given covering the systems $Ca_2B_2O_5$—$CaSiO_3$ and Al_2O_3—Cr_2O_3. The relationships, however, hold only for systems in which ideal solutions are approximated.

In connection with systems of miscible liquids, Litvinov (14, 15) correlated the concepts of Storokin's equation, Raoult's law, and Konoralov's law and later (16) applied the principles to isothermal fractional evaporation and drying problems using general equations for the composition of vapor and liquid phases in ternary mixtures. Pennington (17) presented a relatively simple method for predicting component distribution between two liquid phases in equilibrium. It is applicable to hydrocarbon-solvent systems with sufficient accuracy for engineering design. This method is based on thermodynamic concepts of activity and the formation in hydrocarbon-solvent systems of ideal solutions among the hydrocarbons present. In general, for systems involving paraffins, olefins, and naphthenes, the predictions give good results, but the method cannot be used in the presence of aromatics. Othmer, Ricciardi & Thakar (18) studied the thermodynamic derivations representing vapor-liquid equilibrium conditions in boiling binary systems at constant pressure, using the Gibbs-Duhem equation. This permits the

prediction of vapor composition data from vapor pressure and boiling point data. A similar formula for ternary systems at constant pressure was also presented. Brown & Longuet-Higgins (19) discussed the statistical thermodynamics of multicomponent systems and pointed out that certain complications limit the calculation of thermodynamic properties, making it impossible to use this method alone in evaluating second order terms. Ikeda (20) derived theorems concerning the cluster integrals for the analysis of phase transitions, particularly the condensation of gases. Fournet (21) made a mathematical study of short range order in the case of substitutional solid solutions in metals, while the use of a radioactive indicator in the determination of the solubility of a salt was reported by Jordan (22). This method was tested on Ag_2SO_4 from 40° to 95°C. with good agreement with literature values. It may be used to advantage above the normal boiling point of a solution.

Aqueous Salt Systems

Bullough, Canning & Strawbridge (23) investigated the solubility of ferrous sulfate in aqueous solutions of sulfuric acid at various temperatures from 0° to 100°C. and at acid concentrations of 0 to 50 per cent H_2SO_4. The transition temperature of the heptahydrate to the monohydrate was determined for various acid concentrations. Kunzler & Giauque (24) made some very careful determinations of the freezing point curves of concentrated aqueous sulfuric acid and suggested that the maximum freezing acid is possibly the most accurate standard of acidimetry yet known. Makarov & Chamova (25) studied the system Na_2CO_3—H_2O_2—H_2O at 0°, 10°, and 20°C. and reported the existence of four compounds, $Na_2CO_3 \cdot H_2O$, $Na_2CO_3 \cdot H_2O \cdot 1.5H_2O_2$, $Na_2CO_3 \cdot H_2O \cdot 2H_2O_2$, and $Na_2CO_3 \cdot 2H_2O_2$. No evidence was found, however, of certain other previously reported complexes.

Grubb & Osthoff (26) reported an unusual salting-out effect of hydrohalogen acids (HCl and HBr) on the system dioxane—H_2O. Limits of miscibility for the ternary systems were determined at 25°C. Nardelli & Braibanti (27) investigated the ternary system $Pb(NO_3)_2$—$AgNO_3$—H_2O at 25°C. and found no evidence of complex formation, particularly the previously reported double salt $Pb(NO_3)_2 \cdot 2AgNO_3$. Roy, Roy & Osborn (28) studied the system MgO—Al_2O_3—H_2O at high pressures and temperatures. The transition of brucite to periclase was found to be 475°C. at a pressure of 50 lb. and 670°C. at a pressure of 20,000 lb. per sq. in. X-ray and optical data for both natural and synthetic hydrocalcite and hydromagnesite were also included.

Taylor & Scott (29) made use of a tracer technique, using Cs_2SO_4 as the tracer, to confirm the composition of the compound $Al_2(SO_4)_3 \cdot H_2SO_4 \cdot 12H_2O$ in the system $Al_2(SO_4)_3$—H_2SO_4—H_2O. Later Taylor & Bassett (30) reported a more complete study of the solid phases of this system at 25°, 30°, 50°, and 60° C. with the aid of x-ray techniques. Cavalca & Nardelli (31) studied the ternary system Na_2SO_4—Li_2SO_4—H_2O at 27° and 45.6°C. The double

salt $Na_2SO_4 \cdot Li_2SO_4 \cdot 6H_2O$ was found to exist at both temperatures and up to about 50°C. The anhydrous double salt $Na_2SO_4 \cdot Li_2SO_4$ was present at 45.6°C. No other compound or mixed crystal formation was noted at these temperatures.

Ricci & Fischer (32) found no evidence of solid solution formation in the system thallous sulfate—sodium sulfate—water at 25° and 45°C. in contrast with both potassium and ammonium sulfate—thallous sulfate—water systems previously reported (33). Crystallographic and x-ray studies of the solid phases of the system calcium sulfate—water were reported by Flörke (34), while the reciprocal system calcium sulfate—potassium sulfate—water was studied by Sveshnikova (35) at 55°C.

Sakai, Seiyama & Ikari (36) made further studies of the system HCl—H_2SO_4—Na_2SO_4—NaCl—H_2O in connection with possible methods for the formation of H_2SO_4 and NaCl by double decomposition of Na_2SO_4 and HCl. Tollert (37) reported a dynamic-polythermic investigation of the reciprocal salt pair composed of the sulfates and chlorides of sodium and magnesium. Tests were carried out in an attempt to simulate conditions of deposition of natural salt deposits as opposed to conventional static-isothermal methods.

The system sodium chloride—water at supercritical temperatures and pressures was the subject of a paper by Copeland, Silverman & Benson (38) who describe the apparatus and techniques involved, while Ravich (39) reviewed a number of references on the study of salt equilibria in the presence of steam under high pressure. Also work under high pressure steam was reported by Hansen (40) on the system CaO—SiO_2—Fe_2O_3—SO_3—H_2O in connection with studies of steam-curing of portland cement products.

Solid solution formation between sodium chloride and sodium bromide in aqueous sodium hydroxide solution at 35°C. was studied by Simons, Orlick & Vaughan (41) who found that these two salts form a continuous series of solid solutions with no miscibility gap. This is in disagreement with previous investigators, such as Fineman & Wallace (42) and Hovi & Hyvönem (43).

Guérin & Kozicki (44) reported a study of the copper orthophosphates at 18° and 60°C. The compounds $CuO \cdot 2H_2O \cdot P_2O_5$, $2CuO \cdot 3H_2O \cdot P_2O_5$, and $4CuO \cdot H_2O \cdot P_2O_5$ were found to be stable solid phases, while the compound $8CuO \cdot 8H_2O \cdot 3P_2O_5$, which forms on the addition of phosphoric acid to copper hydroxide, was shown to be metastable and to transform to stable phases on standing.

In regard to aqueous fluoride systems, Talipov & Antipov (45) investigated the solubilities and phase relations in the system CrF_3—NaF—H_2O at 30°C. and found two double salts $3NaF \cdot CrF_3$ and $2NaF \cdot CrF_3$. The same authors (46) also studied the system AlF_3—LiF—H_2O at 25°C. Considerable difficulty with prolonged supersaturation and with colloidal solutions was encountered, while one new double salt ($5LiF \cdot 2AlF_3$) was reported.

Hartford, Costa & Moore (47) studied the solubility of lithium chromate over the temperature range of 0° to 100°C. and found the transition of the dihydrate to the anhydrous form to occur at 74.6°C. The system $K_2Cr_2O_7$—

K_2SO_4—H_2O was investigated between 20° and 40°C. by Bogoyavlenskii (48), while Tananaev & Levina (49) reported considerable work on systems containing the alkali ferrocyanides such as interactions, solubilities, double salt formation, etc., in connection with their use in analytical procedures.

The system potassium arsenate—arsenic acid—water was investigated at 25°C. by Paul *et al.* (50), while Menzel & Müller (51) reported on the system Na_2O—V_2O_5—H_2O at 20°C. In the latter case the results are in disagreement with prior literature, but were confirmed by x-ray studies. Trujillo & Tejera (52) studied the system sodium vanadate—sodium sulfate—water at 25° and found no double salt formation.

Organic Systems

Numerous organic systems having water as one component were reported in the literature during the year. For example, Claussen (53) discussed the solubility of aromatic hydrocarbons in water, while Cymerman & Diamantis (54) determined the partition coefficients between aqueous phosphate buffer solutions and a number of aromatic bases having tuberculostatic activity. The effect of pressure on vapor-liquid equilibria was determined for the system ethyl alcohol—water by Otsuki & Williams (55), while Domansky (56) investigated the system furfural—ethyl alcohol—water. The ternary systems composed of water and 1-propanol together with hexane, heptane, benzene, and 1-butanol were studied by McCants, Jones & Hopson (57). The system isopropyl ether—HCl—H_2O was reported by Campbell, Laurene & Clark (58) at 20°C., while the solubility and phase relations of cobaltous chloride in aqueous tertiary butyl alcohol were studied by Katzin & Ferraro (59). Krupatkin (60) reported closed layering isotherms in the system phenol—phosphoric acid—water in the temperature range of 68° to 100°C., while Taylor & Vincent (61) gave data on phase equilibria in several sulfonic acid—water systems. The system phenylacetic acid—sodium phenylacetate—water at 25°C. was reported by Smith (62). Phase diagrams for the system D-fructose—water for a wide range of temperatures were given by Young, Jones & Lewis (63).

A study of liquid-liquid extraction as applied to four-component systems was reported by Crespi (64) who gave data on the system acetone—$CHCl_2$—acetic acid—water by way of example.

Vapor-liquid equilibria in the system acetone—methanol—water were discussed by Uchida *et al.* (65), while data on the anhydrous system acetone—methanol—ethanol were reported by Amer (66). Hellwig & Van Winkel (67) investigated the vapor-liquid equilibiria for a number of binary systems having ethanol as one component.

The system boron trifluoride—methanol was found by Greenwood & Martin (68) to contain two double compounds (1:1 and 1:2 mole ratios). These are colorless crystalline solids at low temperatures with melting points of −18.6° and −58.1°C. respectively.

Delzenne (69) reported liquid-vapor equilibrium data on the system di-

chloroethane—1,4-dioxane at 1 atm. and on the system methylamine—dimethylamine at 10 atm. pressure, while Kravchenko (70) gave data on several hydrocarbon—dioxane systems.

Liquid-vapor equilibrium relations in the system propane—hydrogen sulfide were reported in detail by Kay & Rambosek (71), and Reamer, Sage & Lacey (72) studied the system pentane—hydrogen sulfide at temperatures from 40° to 340°F. and at pressures up to 4000 lb. per sq. in. In another paper Reamer *et al.* (73) covered the same temperature range for the system decane—hydrogen sulfide up to 10,000 lb. per sq. in.

Kerridge (74) developed melting-point diagrams for certain binary systems of triglycerides. Ravich & Vol'nova (75) studied the phase relations, compound and eutectic formation in the system composed of stearic, palmitic, and oleic acids.

Heterogeneous equilibria in the system *d*-tartaric acid—potassium tartrate were studied and the solid phases characterized by Sartori, Costa & Camus (76). A phase rule investigation of the system *cis*- and *trans*-1,2-cyclohexanediol was reported by Svirbely & Goldhagen (77), while binary systems of the isomeric isoxazole-carboxylic acids were studied by Speroni & Muccini (78).

Several systems containing benzene were reported such as the system acetic acid—benzene by Tan, Krieger & Miller (79), the system ethyl alcohol—1,2-dichloroethane—benzene by Udovenko & Fatkulina (80), and liquid crystals in the binary systems of indene, isoquinoline and naphthalene in benzene by Kravchenko & Pastukhova (81).

Kravchenko & Eremenko (82) reported a mass of detail on the various 2-component systems of fluorene, phenanthrene, anthracene, and carbazole, where in most cases extensive solid solution formation occurred.

The fusion diagram for the system *o*- and *p*-nitrochlorobenzene—chlorobenzene was found to have a ternary eutectic point at −52°C. by Manabe, Honda & Hiyama (83).

The systems mono- and tri-chloroacetic acid—phenol were reported by Udovenko, Airapetova & Malakhova (84). Two stable compounds $CCl_3COOH \cdot PhOH$ (m.p. 37.8°) and $CCl_3COOH \cdot 2PhOH$ (m.p. 31.2°) were isolated and recrystallized from C_6H_6.

The system silicon tetrafluoride—trimethylamine was investigated by Wilkins & Grant (85) who reported the existence of two double compounds (1:1 and 1:2 mole ratios). These both sublimed congruently at about 63°C. at atmospheric pressure, but melted at 81.5° and 89°C. at higher pressures.

Anhydrous Salt Systems

In the reciprocal system of the chlorides and hydroxides of potassium and lithium, Unzhakov (86) reported four double compounds $2KOH \cdot KCl$, $KOH \cdot KCl$, $2LiOH \cdot KOH$, and $LiOH \cdot LiCl$. Kojima (87) studied the ternary system $CeCl_3$—KCl—NaCl, while the systems composed of the mercury halides and the alkali and ammonium halides were discussed in much detail

by Belyaev & Mironov (88). Schäfer & Bayer (89) worked on the system ferric chloride—ferrous chloride and developed a technique for filtration of the eutectic at 297°C.

Several authors reported work on fused fluoride systems, such as an investigation of polymorphism of Na_2BeF_4 (4 modifications) in the system $NaF—BeF_2$ by Roy, Roy & Osborn (90) and studies in the binary systems $CaF_2—BeF_2$, $MgF_2—BeF_2$, and $LiF—MgF_2$ by Counts, Roy & Osborn (91). The systems $KF—MgF_2$ and $AgF—ZnF_2$ with the double salts $KF \cdot MgF_2$, $2KF \cdot MgF_2$, and $AgF \cdot ZnF_2$ were investigated by DeVries & Roy (92). Wagner & Balz (93) gave data on the system $KF—NiF_2$ and the double compounds $KF \cdot NiF_2$ and $2KF \cdot NiF_2$. Portions of the fused system composed of the fluorides, chlorides and chromates of sodium and potassium were reported by Rassonskaya & Bergman (94).

A study of the system $Ag_2HgI_4—Cu_2HgI_4$ was reported by Suchow & Keck (95), while the systems $NaCl—SrSO_4$ and $NaCl—BaSO_4$ were investigated by Byé & Holder (96). Plyushchev & Komissarova (97) gave new data on the system $Li_2SO_4—CaSO_4$ with a eutectic at 695°C., while the reciprocal system sodium—lead sulfates and tungstates was studied by Belyaev (98) who also worked with Nesterova (99) on the parallel system involving potassium in place of sodium.

The ternary system sodium sulfate—chromate—nitrate and the corresponding potassium system were reported by Rassonskaya & Bergman (100).

Morey (101) studied the system composed of the metaphosphates of sodium and calcium and reported a double salt $4NaPO_3 \cdot Ca(PO_3)_2$ melting congruently at 738°C. Eutectics between the two single salts and the double salt occur at 625° and 725°C.

Belyaev & Sholokhovic (102) gave data for portions of the system sodium—potassium—barium carbonates and titanates up to 1200°C., while phase reactions in the system sodium carbonate—sodium silicate were studied by Moriya, Sakano & Tatsumi (103). Nonmiscible liquid equilibria in the system $Na_2O—Al_2O_3—SiO_2—Ca_3(PO_4)_2$ were studied by Melent'ev & Ol'shanskii (104).

A detailed study of complex formation in the ternary systems composed of the sulfates, tungstates, and metaborates of lithium and potassium was carried out by Bergman, Kislova & Posypaiko (105), while Reshetnikov & Diogenov (106) reported on certain irreversible features in the reciprocal system of potassium and lithium chromates and hydroxides.

Metallic Systems

Metallic systems in which aluminum was one component received considerable attention during the year. Trillat & Takahashi (107) found that films of 60 per cent Cu and 40 per cent Al deposited on cold surfaces by evaporation and condensation under vacuum immediately transformed to crystalline mixtures of Al_2Cu and AlCu. A critical review of contradictory

data on the system aluminum—magnesium was published by Eickhoff & Vosskühler (108), while Urazov & Mirgalovskaya (109) also attempted to correct discrepancies in previous work on the ternary system Al—Mg—Cu. Phillips (110) gave data on solid solution and eutectic formation in the system Al—Cu—Si and Komatsu (111) reported metallographic research on the system Al—Cu—Si—Mn, but found no quaternary compound present.

Saito (112) presented a new phase diagram for the ferromagnetic range of aluminum—iron alloys, showing a new compound Al_5Fe_{13}. Gebhardt (113) reported the use of a centrifuge to separate the eutectic for analysis in the system Al—Fe—Zn, while Armand (114) made a detailed study of the system Al—Fe—Si and characterized the various solid phases.

The system aluminum—zirconium was found by McPherson & Hansen (115) to be relatively complex with nine intermediate phases in addition to eutectics and solid solutions. Davies (116) reported data on the immiscibility region in the system Al—Pb—Sn at 650°, 730°, and 800°C. The systems Al—Ge—Na and Al—Ge—Li were studied by Boom (117) and the system Al—Cr—Ti was discussed by Taylor & Duwez (118).

As might be expected, references to work on systems of iron alloys were also quite numerous during the period of review. The systems iron—arsenic and iron—arsenic—carbon were reported by Sawamura & Mori (119). McBride, Spretuak & Speiser (120) studied the system iron—ferroboron and showed that boron forms an interstitial solid solution in γ-Fe, but a substitutional solid solution in α-Fe. The system Fe—S was investigated by Grønvold & Haraldsen (121) in connection with a study of phase relations of synthetic and natural pyrrhotites, while Nichols (122) made an equilibrium study of the system Fe—S—O from 1555° to 1645°C. The system Fe—FeS—FeO from 1140° to 1400°C. was reported by Ol'shanskii (123).

A system of importance in the metallurgy of copper sulfide ores, namely, the system Cu—Fe—S, was the subject of a study by Schlegel (124), while a series of phase diagrams for the portions of the Co—Fe—S system were published by Vogel & Hillner (125).

Van Thyne, Kessler & Hansen (126) developed isotherms at a number of temperatures for the system Fe—Cr—Ti and reported a ternary eutectoid at about 540°C. containing 8 per cent Cr and 13 per cent Fe. Phase relations in the ternary systems Fe—Cr—W and Fe—Cr—Mo and the existence of the compound Fe_3CrMo_2 were studied by Goldschmidt (127) using x-ray powder diffusion methods. Portions of the systems Fe—Ni—Mo and Fe—Co—Mo were surveyed by Das & Beck (128) at 1200°C. using x-ray diffraction and etching methods, while the system Fe—Cr—Mo was explored by McMullin, Reiter & Ebeling (129) who showed the existence of the compound Fe_3CrMo.

The diagram of state for the system iron—iron phosphide—molybdenum phosphide—molybdenum was developed by Vogel & Hortmann (130), while studies of carbide phases in various alloy steels were reported by Kuo (131). Data on the system iron—manganese was given by Yoshisaki (132) and on

the system iron—manganese—carbon by Isobe (133) who also reported an investigation of the binary system Mn—C (134).

The constitution of chromium—manganese alloys below 1000°C. was the subject of a paper by Pearson & Hume-Rothery (135).

In regard to nickel alloys, Lihl (136) investigated the system Ni—Zn and Scheil & Hütter (137) found a ternary compound of uncertain composition in the system Ni—C—Mg. The systems Ni—Cu—Mg, Ni—Zn—Mg, and Mg—Zn—Cu were studied between 500° and 1200°C. by Lieser & Witte (138).

The system lead—magnesium—zinc, of importance in diecasting, was explored by Obinata & Miura (139), while the known phase diagrams for the systems Pb—Cd—Bi and Pb—Sn—Bi were corrected by Ho, Hofmann & Hannemann (140) to show the presence of the hexagonal Pb—Bi β-phase. No ternary compound was found in the system Sb—Sn—Bi by Vogel & Apel (141).

Equilibrium conditions between zinc—silver alloys and zinc vapor were studied by Scatchard & Westlund (142) and the phase diagrams and lattice constants of the alloys of cobalt with rhenium, ruthenium, osmium, rhodium, and iridium up to 2500°C. were published by Köster & Horn (143). The platinum—mercury amalgams were investigated by Bauer, Nowotny & Stempfl (144) who reported three compounds, PtHg, $PtHg_2$ (tetragonal), and $PtHg_4$ (cubic).

Work on silicon systems included an investigation of the disilicides of Cr, Mo, W and Ti by Nowotny, Kieffer & Schachner (145), the system tantalum—silicon by the same authors plus Benesovsky (146) and the system tungsten—silicon by Kieffer, Benesovsky & Gallistl (147).

The metal indium came in for its share of attention by such authors as Grinstead & Yost (148) who made a detailed study of ferromagnetic alloys in the system Cu—Mn—In. Data on the systems In—Sb and In—As were reported by Liu (149) and the system InAs—InSb was explored by Shih & Peretti (150). They system indium—manganese was studied by Valentiner (151) who found the Curie temperature to be about 300°C. while Gebhardt & Dreher (152) studied the system copper—silver—indium up to an In content of 30 per cent.

The system copper—manganese—tin was found by Valentiner (153) to contain two ternary compounds, Cu_2MnSn at higher temperatures, transforming on cooling below 400°C. to Cu_3Mn_4Sn which is stable at room temperature. The solid solution area of this system was explored by Funk & Rowland (154) at various temperatures from 350° to 750°C. Other copper alloy systems, such as Cu—Ge by Schubert & Brandauer (155) and Cu—Ce by Byström, Kierkegaard & Knop (156) were also noted in the literature.

Rostoker & Yamamoto (157) reported a survey of 21 binary systems having vanadium as one component, while the vanadium—uranium constitution diagram, showing no intermediate phases, was given by Saller & Rough (158). The titanium—carbon phase diagram was found by Cadoff & Nielsen

(159) to have a peritectic point at 1750° and a peritectoid point at 920°C. The titanium—tungsten and titanium—tantalum systems were studied by Maykuth, Ogden & Jaffee (160) while the system titanium—manganese was also reported by the same authors (161). Phase studies in the system titanium—tantalum—carbon were made by McMullin & Norton (162) but no ternary compound was noted.

The zirconium—nickel phase diagram up to 40 per cent Ni was published by Hayes, Roberson & Paasche (163), while the zirconium—boron system was the subject of a paper by Glaser & Post (164). Nowotny & Schachner (165) made x-ray studies of the systems Zr—Sn and Zr—Pb and reported a compound Zr_5Pb_3 and a Zr—Sn compound of uncertain composition.

The system thorium—manganese was shown to contain three solid phases $ThMn_2$, Th_6Mn_{23} and $ThMn_{12}$ according to Florio, Rundle & Snow (166), while the system beryllium—uranium yielded one intermediate compound UBe_{13} as reported by Buzzard (167).

Oxides and Refractory Systems

The region of nonrefractory compositions (melting below 1600°C.) in the system calcium oxide—magnesium oxide—aluminum oxide was explored by Repenko (168), while the formation of dicalcium ferrite and of solid solutions in the system calcium oxide—ferric oxide—aluminum oxide was studied by Cirilli & Burdese (169). Both brownmillerite and the previously reported compound $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$ were shown by x-ray and crystallographic methods to be members of a series of solid solutions. These authors also studied phase transitions occurring in the reduction of calcium ferrites at various temperatures (170, 171).

Data on the system FeO—SiO_2 and the formation of fayalite ($2FeO \cdot SiO_2$) were given by Naruse & Sugimura (172). It was shown that reaction $2FeO + SiO_2 \rightarrow$ fayalite was 20 per cent complete at 900° and 90 per cent complete at 1050°C. Phase diagrams for the system FeO—Fe_2O_3—SiO_2 at slag forming temperatures (1250° to 1450°C.) were reported by Schuhmann, Powell & Michal (173) who discussed the significance of the results from the standpoint of their importance in copper smelting.

Agamawi & White (174) gave a number of isotherms between 1500° and 1700°C. for the system Al_2O_3—TiO_2—SiO_2, while the same authors (175) also reported a great deal of data on the quaternary system CaO—Al_2O_3—TiO_2—SiO_2 in connection with the formation of the minerals anorthite and sphene.

Phase relations in the ternary system Na_2O—P_2O_5—SiO_2 were studied by Turkdogan & Maddocks (176) who reported a stable compound of composition $9Na_2O \cdot 2P_2O_5 \cdot 6SiO_2$ (m.p. 1100°) and two peritectic compounds, $5Na_2O \cdot P_2O_5 \cdot 4SiO_2$ (m.p. 953°) and $15Na_2O \cdot 5P_2O_5 \cdot 6SiO_2$ (m.p. 987°C.).

In the system calcium oxide—chromium sesquioxide, x-ray investigations by Burdese (177) showed the binary compound $CaCr_2O_4$ to have two crystal-

line forms, the β-(rhombic) form converting to the α-(tetragonal) form upon heating above 1900°C.

X-ray diffraction studies of gels in the system Al_2O_3—SnO_2—TiO_2 were carried out by Milligan & Holmes (178). The gels were prepared by adding water to alcoholic solutions of the alcoholates. The precipitates were then dried and heated to higher temperatures for 2 hr. prior to examination. At 800°C. an unidentified Al_2O_3—TiO_2 compound was noted, but above 1000°C. no samples remained amorphous and the only TiO_2 phase was rutile.

The uranium oxide systems UO_2—Al_2O_3 and UO_2—MgO were reported by Lambertson & Mueller (179) who found no solid solutions or compound formation. Epstein & Howland (180) studied the binary systems of UO_2 with a number of other oxides and found that the compositions of the eutectics could be calculated on the basis of ideal solution laws with satisfactory agreement with experimental data.

The system ZrO_2—SiO_2 was studied by Curtis & Sowman (181), while considerable work on the system MgO—ZrO_2—SiO_2 was reported by Berezhnoi & Karyakin (182, 183) some of the results of which were found to be in conflict with prior investigators. Finally, a detailed survey of a large number of binary systems, having ZrO_2 as one component, was made by Dietzel & Tober (184) who quoted x-ray analyses and crystal lattice structures for many of the systems discussed.

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SOLUTIONS OF ELECTROLYTES[1]

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This chapter differs somewhat from previous ones in this series in considering only a small fraction of the many papers which would, on a different plan, have come up for review. The reason for this departure is that several of the 1953 papers turned out to be of such unusual interest in their bearing on the still vexed question of the state and behavior of ions and water molecules in aqueous electrolytes, as to make it seem desirable to discuss them at some length. Because of space limitations, the decision to do so has made it necessary to omit even the mention of the great majority of publications dealing with ionic solutions which have appeared during the period under review, a necessity which we regret. It has also restricted us once more to aqueous systems, in fact, even to the "simpler" members of this class. There are still many gaps, however, in our understanding of these systems and we have felt that the papers which are here discussed would repay the more extended consideration which we have given them. There is, to be sure, a large subjective element in essays of this kind. For example, our own interest in structural interpretations will be readily apparent in the present chapter. We have made no effort to avoid this, expecting that over a period of years the vector sum of the personal slants of a succession of reviewers will determine a correct direction for the series as a whole.

Part One

The appearance during 1953 of two papers by Poirier (1, 2), under the title "Thermodynamic Functions from Mayer's Theory of Ionic Solutions" was an event of more than ordinary significance for electrolyte theory, although the "practical" result was confined to calculation of activity coefficients in aqueous solutions of NaCl up to about $0.4M$, in $CaCl_2$ up to about $0.1M$ and in $ZnSO_4$ and $LaCl_3$ to concentrations no higher than $0.01M$. The value of Poirier's work, transcending these restrictions to the "slightly polluted water" range of composition, lies, in part, in the fact that these are the first precise numerical calculations of electrolyte activity coefficients ever to be made (so far as the present reviewers are aware) from equations which do not have the Debye-Hückel (3) theory as their starting point, and which are free, therefore, from the physical and mathematical criticisms to which that theory is subject (4). In part, also, it lies in the excellence of the agreement between calculated and experimental values in the cases presented, as

[1] The survey of the literature pertaining to this review was concluded in December, 1953.

[2] The preparation of this review was supported in part by the Office of Ordnance Research.

well as in the way in which certain qualitative features of experimental $\log f_{\pm}$ versus $c^{1/2}$ curves (turning up after a minimum for some I-I, II-I, and III-I salts; falling below the limiting law slope in dilute solutions of II-II salts in certain cases) are reproduced without recourse to additional parameters or *ad hoc* assumptions. Not least in importance, however, is that these papers bring Mayer's theory (5) to a "pay-off" stage where the simplicity of its model, and the rigor of the method by which the model is treated, can be applied to the gaining of authentic new insights into the nature of ionic solutions.

Mayer's paper (5), from which this work stems, considers a solution of ions in a dielectric solvent, adapting to this case the method previously worked out (6, 7) in general for obtaining the osmotic pressure in a liquid solution from the (known or assumed) potential of average force between the solute particles. The procedure employs the same formalism as is used in evaluating the virial coefficients of a gas (8) as integrals, in which the integrands are sums of products occurring in the expansion of the exponential of the potential energy (here the potential of average force).

Essential to the whole calculation is the assumption that the total potential of average force for all of the solute is representable as a sum of pair-energies; that is, that

$$W_n = \sum_{n \geq i > j \geq 1} w(R_{ij})$$

This involves the explicit assumption that the potential of the interaction between any two ions is dependent only on the distance separating them and is, in particular, unaffected by the position of any other ion. This is certainly true for coulombic interactions in a dielectric medium, which are what Mayer assumes, but the point will be worth returning to later on.

The pair potential assumed is

$$w(R_{ij}) = (Z_i Z_j e^2/KR_{ij}) \exp(-\alpha R_{ij}) + w^*(R_{ij}) \qquad \text{II}$$

where Z_i and Z_j are the valences of the relevant ions and R_{ij} their distance apart. K is the dielectric constant, α an auxiliary parameter and $w^*(R_{ij})$ is a short-range repulsive potential, taken care of in the sequel by assuming a "cut-off distance," outside of which w^* is zero, and inside of which the ions are not permitted to penetrate (i.e., the integrals are not allowed to extend). This corresponds qualitatively to a hard sphere diameter and also prevents the mathematical catastrophe of an infinite integrand at $R=0$. The "cut-off distance," as expected, shows up as a parameter in the final expressions for activity coefficient and osmotic pressure.

The exponential $e^{-\alpha R}$ is introduced as a device to circumvent the other customary difficulty, namely, divergence of volume integrals of coulomb energies as $R \to \infty$. This factor makes the integrals converge as first set up, and a very ingenious treatment involving classification and separate consideration of different categories of sums and products in the integrand proves that they stay civilized as α approaches zero. The terms retained in

the summation therefore do not contain α. They are carried far enough in this work to give expressions in c (molar concentration) which are correct up to and including terms of order $c^{3/2}$. It is concluded that these account for the effects of all of the long-distance interactions of the ions, as well as for those of the short-distance interactions of all pair types, including the influence on the latter arising from the long-range electrostatic potential of any third ion in the neighborhood. The terms which are neglected include the effects of very close interactions of three or more ions.

The final results obtained by Mayer are expressions for log $f_\pm$ and for osmotic pressure, given in terms of explicit functions (which are convergent sums of definite integrals) of $c^{1/2}$. These expressions reduce to those of the Debye-Hückel limiting law at infinite dilution, and at higher concentrations contain only one specific parameter, namely, the cut-off distance referred to above.

The activity coefficient so calculated, however, can not be compared directly with experimentally measured activity coefficients since it refers, not to a solution which is at standard pressure, but to one which is at a total pressure (variable with composition of solution) equal to the standard pressure plus the osmotic pressure of the solution. This is because of the nature of the underlying theory which treats the solvent as being at constant activity, regardless of the concentration of the solute, a condition which must be interpreted physically by imagining that as solute is put in an extra pressure is exerted from outside equal to the osmotic pressure. This means that to get a value of ln $f_\pm$ for comparison with experiment, the ln f' given by Mayer's equation must be "corrected down" to one atmosphere. It also means that the osmotic pressure plays a unique role in this theory, since it must be used (in principle) in the correction process involved in calculation of any other thermodynamic quantity. (In practice the corrections to $\overline{L}_2$ and $\overline{V}_2$ are found to be negligible.)

Poirier has now taken the formidable mathematical and thermodynamic complexity of the Mayer theory and evolved from it a manageable procedure for arriving at calculated numerical values for the thermodynamic quantities: P_{osm} (osmotic pressure), ln $f_\pm$, $\overline{V}_2$, $\Phi(V)$, $\overline{L}_2$, and $\Phi(L)$. For this purpose he has tabulated the numerical value (to 6 or 7 figures) for the coefficient of each successive term (up to 16 terms) for each of the three sum functions for which values are needed. These are tabulated for various values (30 to 50 entries) of a quantity φ, which is the product of a, the cut-off distance, and κ, the same κ that occurs in the Debye-Hückel theory, defined as

$$\left(\frac{4\pi e^2}{\kappa kT}\cdot\frac{Nc}{1000}\cdot\sum_i \nu_i Z_i^2\right)^{1/2}.$$

The quantity φ, and therefore all of the sum functions, are thus determined by concentration; the numerical values also depending on the temperature, the dielectric constant of the solvent, the valence type of the salt (which also

enters the make-up of the sum functions), and the cut-off distance. After evaluation, and usually after interpolation, the sum functions are used in prescribed ways to get calculated values for the thermodynamic functions. The prescription may call for use of additional constants representing properties of the solvent or solute. Thus, calculation of $\overline{V}_2$ and $\Phi(V)$ requires values for β_1, the compressibility of the solvent, $(\partial K/\partial P)_T$, the pressure derivative of the dielectric constant, and $\overline{V}_2^\circ$, the partial molal volume at infinite dilution of the salt. Because of the above mentioned need to correct down to standard pressure, these same three constants (one of them specific) are involved also in final calculated values of $\ln f_\pm$.

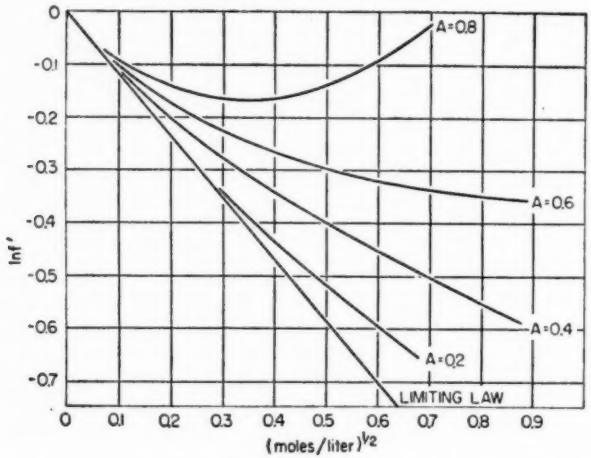

FIG. 1. $\ln f'$ versus $c^{1/2}$ for I-I salts according to Mayer's theory. Reproduced by permission of J. C. Poirier and the *Journal of Chemical Physics*.

The pressure correction is important when precise calculations are required for comparison with precise experiments (four figures in $\ln f_\pm$), but is small enough not to affect the qualitative course of the $\ln f_\pm$ versus $c^{1/2}$ curves which, for water at 25°C. and without this correction, are shown in two of Poirier's figures which are reproduced below (Figs. 1 and 2). In these, $A = aKkT/\hat{e}^2 (\equiv a/7.13458$ for water at 25°C., Å in $a)$ and the way in which $\ln f_\pm$ passes through a minimum and then turns up for I-I salts with large A while negative deviations from the limiting law are shown by II-II salts with small A is particularly striking in view of the known trends of this nature displayed by experimental curves for real salts. (Similar, but much smaller, negative deviations are also shown by the theoretical curves for I-I salts when A is as small as 0.2.) Before discussing these curves further, however, we present Poirier's comparison between observed and calculated

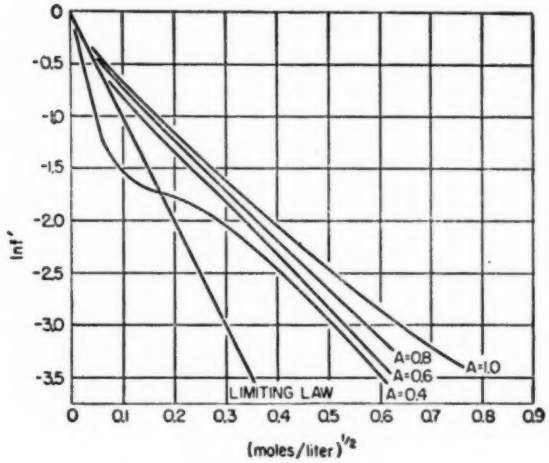

FIG. 2. $\ln f'$ versus $c^{1/2}$ for II-II salts according to Mayer's theory. Reproduced by permission of J. C. Poirier and the *Journal of Chemical Physics*.

values of $\ln f_{\pm}$ for NaCl. The calculation was made by ascertaining, by successive approximation (Poirier gives auxiliary tables to aid in this process), the value of A which would give a calculated value in exact agreement with experiment at $0.10M$. This value of A (0.5464; $a = 3.898$ Å) was then used to calculate values of $\ln f_{\pm}$ for the other concentrations whose experimental values were reported. The success of this comparison, shown in Table I, is no less spectacular than that of the qualitative results just mentioned. Above $0.4M$ (and for higher valence types the agreement does

TABLE I

THE QUANTITY $\ln f$ FOR NaCl IN AQUEOUS SOLUTION AT 25°C.

Molarity	$\ln f_{\text{expt1.}}$	$\ln f_{\text{theoret.}}$	$\ln f_{\text{expt1.}} - \ln f_{\text{theoret.}}$
0.004984_9	−0.0744	−0.0754	0.0010
0.009967_0	−0.1016	−0.1025	0.0009
0.019934_4	−0.1363	−0.1372	0.0009
0.03985_5	−0.1798	−0.1801	0.0003
0.05976_2	−0.2084	−0.2089	0.0005
0.07965_5	−0.2307	−0.2310	0.0003
0.09952_4	−0.249	−0.249	0.000
0.1986_8	−0.306	−0.309	0.003
0.2974_7	−0.337	−0.347	0.010
0.3959_0	−0.359	−0.374	0.015

not go much beyond 0.01 M) the accuracy drops off, possibly due to the onset of effects of ion triples, etc., which Mayer stated were not included in his sums, but possibly also for other reasons.

The range of "good fit" for NaCl and the other salts treated, while limited, is wide enough to permit the use of this formalism in drawing important conclusions about the physical nature of ionic solutions. These conclusions will, in many cases, be confirmations of what is already believed, or clarifications of existing interpretations. This can be seen by considering, first, an idealized solution of hard sphere ions of a single size immersed in a solvent which is an idealized dielectric medium. Such a system will be exactly described by the equations, since the latter are the result of a rigorous mathematical treatment of exactly this model. The fact that the equations give an initial decrease in $\ln f_{\pm}$ which is identical with that of the Debye-Hückel theory in the limit of infinite dilution, confirms the belief that the Debye-Hückel ion cloud has the meaning and effect usually accepted for this case. On the other hand, the fact that this model can give upward deviations from the limiting law line, leading in some instances to positive slope of the $\ln f_{\pm}$ versus $c^{1/2}$ curve, or even to positive values of $\ln f_{\pm}$, means that such upward deviations need not be attributed either to hydration or to change in dielectric constant with composition of solution, for these two influences were deliberately omitted in the formulation of the model. This is an important new result, since such additional physical assumptions have been customarily made in explaining the rise. On this model the cause is more probably an exclusion effect, qualitatively similar to that suggested by Van Rysselberghe & Eisenberg (9) or by Wicke & Eigen (10), which takes into consideration interference of a "cloud" ion with other "cloud" ions rather than with the "central" ion only, which is all the Debye-Hückel parameter a can provide for.

Again, the negative deviations produced by the Mayer model at low concentrations of I-I and II-II salts with small ions is doubtless a "built-in" provision for association of the Bjerrum (11) type. [Such association is also provided for, though at the cost of mathematical self-consistency, by the Gronwall-LaMer-Sandved "higher terms" extension (12) of the Debye-Hückel theory.] This confirms the supposition that nearest-neighbor ion pairs are effective in lowering activity, whether they be produced by purely electrostatic effects or arise from "chemical" interaction, and is a useful reminder that "strong electrolytes" are not necessarily "100 per cent dissociated" in any meaningful sense.

One of Poirier's most valuable contributions is the presentation of his tables and procedures in a form which other people can use. This has made it possible for one of us (13) to discover that the a values which must be assigned to 0.1 M solutions of the various alkali halides to give agreement with the activity coefficient data quoted by Harned & Owen (14) bear the same peculiar relationship to the generally accepted ion sizes as do the Debye-Hückel a's (15). For example, the a values assigned for cesium salts

are less than the crystallographic radius sums (16); e.g., for CsCl, $a = 3.176$; radius sum, $1.69 + 1.81 = 3.50$ Å. Since Poirier reports for NaCl that $a = 3.90$ Å as compared with the crystallographic radius sum 2.76 Å, it appears that, in so far as the crystallographic radii are correct hard-sphere radii for solutions of this sort, the behavior of the solutions is different from that described by the model. This also illustrates the statement made by Mayer and repeated by Poirier that the a of this theory is in part a proper hard-sphere diameter, and in part a "catch all" in which will appear the effects of anything in the model which is unrealistic.

What is apparently happening in the NaCl solution is that the actual number of close or medium-range encounters of anion and cation is smaller (as compared with frequency of occurrence of greater separations), than that called for by the simple model, thus producing too large an average distance of separation. This, in turn, produces an activity effect which, in this formalism, is represented by too great a cut-off distance. On the other hand, it would appear that, in CsCl, there are more of the closer encounters occurring, comparatively, than the model would predict, producing too small an average distance of separation and too small an a. The former state of affairs could be accounted for by the inability of Cl^- to penetrate a hydration shell around Na^+, and this assumption (which is the one usually made) would agree with the fact that Li^+, which is thought to be more heavily hydrated than Na^+, appears in LiCl with an a value which is in still greater excess over the crystallographic radius sum. An excessive number of comparatively close encounters in CsCl might well be expected, in the absence of hydration, from a lowering of dielectric constant in the immediate neighborhood of an ion as a result of dielectric saturation of the water (17, 18).

It should be pointed out that in considering hydration in any treatment based on the Debye-Hückel distribution function, two separate kinds of consideration are necessary, while in the Mayer theory the single act of making a larger corresponds to both of them. This is because Mayer, in evaluating a configuration integral, considers both the electrostatic (coulombic) and the nonelectrostatic ("effective quantity of solvent") effects, so that an "artificial" increase in a accounts for both the weakening of electrostatic forces and the removal of some of the water from its solvent function (i.e., for the inaccessibility of a part of configuration space). In the older treatment an increase in the Debye-Hückel a did only part of the trick, the rest requiring a Bjerrum hydration correction (19). (As noted in a later section, it is possible to "improve" the Debye-Hückel distribution function in a way that makes the Bjerrum correction unnecessary.)

This "both in one" feature of the Mayer theory may account for the somewhat surprising result that whatever hydration may be occurring in NaCl does not seem to disturb the accuracy of the fit of calculated-to-observed concentration dependence of $\ln f_{\pm}$ (cf. Table I). Actually, the fit must be assumed not to be perfect, for it can also be shown (13) that the apparent relative molal heat content, $\Phi(L)$ of NaCl, computed from Poirier's

equations and tables and using his a for NaCl, is far from precise in its fit with the data of Robinson (20). The only new disposable constant in $\Phi(L)$ is $\partial \ln a/\partial T$, and this was chosen to force a fit at $0.1M$. Alternatively, it is possible to find at each of several concentrations the value of $\partial \ln a/\partial T$ which fits the data, and this series of values turns out to be concentration dependent. This means that a itself must have some concentration dependence. If this dependence is of the form $a=a_0+a_1c$, it is readily conceivable that we could simultaneously have $a_0 \gg a_1$ and $\partial a_1/\partial T \gg \partial a_0/\partial T$. In the light of this finding it is not surprising to have it turn out that in the case of $\ln f_\pm$ for LiCl, neither the data of Robinson & Sinclair (21) nor those of Scatchard & Prentiss (22) seem (13) to be representable by this theory to as high a precision as that to which the data are reported. It also appears that, as concentration increases from low values, discrepancies between observed and calculated values for $\ln f_\pm$ may arise because of different concentration dependence of supplementary (nonmodel) effects rather than from the overstepping of the concentration range for which the integration is valid. This would be in harmony with the fact that Mayer (5) seems to have expected the range of validity of the integration to be wider than what is now observed as a range of good fit.

While the conclusions we have drawn from the behavior of empirical a values derived from this theory do not differ from those suggested by the a values of earlier theories, we feel that the superior rigor of the Mayer derivation has made possible a real advance in the following sense: disagreement between results calculated from a model and results of reliable experiments has always meant either something wrong with the model or something wrong with the way in which the model was treated; therefore, the more confidence we can have in the treatment, the more confidence we can have in inferences about the model (and thus about the reality which the model is designed to imitate).

Part Two

An unconventional but very stimulating alternative point of view in interpreting the different a values displayed by the different alkali halides (i.e., relative order in which $\ln f_\pm$ values fall) is presented in the book "Ionic Processes in Solution" by Gurney (23) which also appeared during the year under review. This book is partly monograph and partly text-book, and is properly referred to here by reason of some novel ideas it contains which do not seem to have appeared in journal articles. One of these (p. 255) states that the distance of closest approach of an anion and a cation in aqueous solution should be expected to be greater than the corresponding crystallographic radius sum by something in excess of 1 Å. The qualitative reasoning is that, since the internuclear distance in a crystal is determined by the balance of cohesive and repulsive forces, the corresponding distance in solution should be larger because the smaller cohesive force will produce a balance at an increased separation. Quantitatively, however, Gurney seems

to overdo the increase by taking the attractive force between ions in "contact" in aqueous solution to be $Z_+Z_-\epsilon^2/K r^2$ where K is about 76, the macroscopic dielectric constant of water. This makes too small an attraction, partly because of the coarse-grained structure of the water on this scale, and partly because of the saturation of dielectric polarization (17), and causes Gurney to have to go too far out to find the point at which the repulsive force has suffered the same decrement. In spite of such quantitative criticisms, it is doubtless true that the expected actual distance of closest approach in solution should be appreciably greater than the crystallographic radius sum. Referring to the examples given above, this would intensify the need to explain the small a for CsCl, and decrease the apparent amount of hydration in NaCl, though probably not account for the full increase in a in this case.

The most novel thing Gurney has done is to correlate "the observed facts as to activity coefficients . . . with known behavior of the ions as regards viscosity and entropy" (p. 257) through the concept of structure-forming or structure-destroying tendencies of different ions. He traces this concept to Cox & Wolfenden (24) who used it in 1934 to explain the sign of the "linear term" in the viscosity-concentration relationship of aqueous salt solutions in terms of the Bernal & Fowler (25) picture of water structure. In the equation connecting the experimentally measured viscosity of a salt solution with its concentration, the "linear term" is the term representing the specific influence of the solute, as opposed to the general square-root term which expresses the (small) initial rise in viscosity due to Debye-Hückel type interaction (26). Salts like KCl, for which the linear term is negative, i.e., which decrease the viscosity, are considered to have a net structure-breaking effect, whereas LiCl, with a positive linear term representing a specific viscosity-raising influence, is supposed to have a net structure-promoting effect. Gurney, following Cox and Wolfenden, notes that the ions which lower viscosity are the ones with high ionic mobility and low temperature coefficient of mobility [(27) p. 70], whereas the ions of low mobility, which also have high temperature coefficients of mobility, are the ones which specifically increase viscosity. (High temperature coefficient is taken to mean a large amount of "ice-like" structure, which "melts" as temperature is raised.) He also correlates these effects with the conventional partial molal entropies of the ions which he has earlier considered in a discussion of the entropies of solution of solid alkali halide salts.

Frank & Evans (28) had previously used entropy data to derive an interpretation of structure effects of ions which is very similar to the interpretation Gurney has presented. This postulates that, in addition to the "freezing" of water in the strong field in the immediate neighborhood of an ion, there must be a "thawing" of water structure at somewhat greater distances to account for the smallness of the entropy loss when a hypothetical gas ion is brought into solution. Therefore, depending on the extent to which freezing takes place (and therefore on the ionic charge and radius) the net disturbance

of water structure may end up as an increase or a decrease in over-all structural tightness, producing a net negative or positive structural entropy change. Frank and Evans correlated this with viscosity results [using the tabulation of Bingham (29)] and also with the order of partial molal heat capacities at infinite dilution (30), suggesting that $\overline{C}_{p2}^{\circ}$ of KCl, for instance, is -29.0 cal/deg/mole as compared with -16.2 for LiCl because around the K^+ ion there is less "ice-like ness" left to melt as temperature rises, absorbing less heat and making $\overline{C}_{p2}^{\circ}$ more negative. Gurney goes farther than Frank and Evans did in proposing a plausible mechanism for the structure-breaking effect, which he attributes to a competition between the orienting influence on a given water molecule of the ion on the one hand, and its water neighbors on the other. His picture differs from theirs in another respect also, in that he apparently considers that structure-forming and structure-breaking are alternative influences which an ion can exert on the water molecules in immediate contact with it, whereas Frank and Evans represented these immediate water neighbors as being always "frozen" and located the "melting" at greater distances from the ion.

Parenthetical mention should be made at this point of two other treatments of the influence of ionic solutes on water structure. These are given by Haggis, Hasted & Buchanan (31) and by Eucken (32), on the basis of two rather definite but very different sets of assumptions regarding the nature of water itself. The former treatment is, in general, compatible with the picture outlined above and is based on studies of microwave absorption in water and aqueous solutions, from which solute influences on static dielectric constant and on relaxation wavelength are computed. It has been used by Hasted & El Sabeh (33) in a 1953 paper, in which microwave measurements on salt solutions are reported over a temperature range from 0° to 60°C. We greatly regret that space limitations make it impossible to report this work more fully. To the Eucken treatment we shall refer later in this review, returning now to Gurney's quite different line of thought.

This proceeds with the idea that some ions, with respect to a variety of properties, give evidence of having a net structure-breaking, some a net structure-forming effect upon the solvent water, the former being large univalent ions and the latter small or multiply-charged ones. Among the alkali metal ions the sequence, as expected, from the strongly structure-forming to the strongly structure-breaking is Li^+, Na^+, K^+, Rb^+, Cs^+, with the zero just before K^+. Among the halide ions, F^- is a structure-former, and the others progressively stronger structure-breakers, from Cl^- to I^-. On grounds of viscosity, OH^- and CH_3COO^- are also structure formers and NO_3^- a strong structure breaker. Gurney now makes the bold suggestion that these influences furnish a key to the long-known (34) regularities of trend of $\ln f_{\pm}$ values (at constant concentration) wherein (*a*) for lithium, sodium, and potassium salts, iodides lie above bromides, bromides above chlorides, and chlorides above fluorides, whereas for rubidium and cesium salts this order is reversed; and (*b*) for chlorides, bromides, and iodides,

lithium salts lie above sodium, sodium above potassium, etc., whereas for fluorides the order is reversed. Hydroxides and acetates act like fluorides while nitrates act like bromides or iodides. He points out that the reversals in these activity effects correspond to reversals in structure-making or breaking influence, and adds

"if we follow the succession of curves [of $\log f_{\pm}$ vs. $c^{1/2}$] from top to bottom [e.g. from NaI to NaF or from CsF to CsI] we go from ions of dissimilar character to ions of similar character"

(in respect to structural influence, p. 259). In point of fact, there is apparently some crossing in the experimental curves of $\ln f_{\pm}$ versus $c^{1/2}$, so that the order at low concentrations may not be as regular as the typical order described for high concentrations. This makes the situation somewhat less simple than Gurney has assumed. On the other hand, his correlation predicts an irregularity which, on examination, is proven actually to exist. The prediction is that for the potassium halides the decrease from iodide through chloride should be followed by an increase again to fluoride, as K^+ is near zero in structural influence, and so is Cl^-. Thus, among the halide ions Cl^- is most similar to K^+, so that KCl should have the lowest activity-coefficient curve of any of the potassium halides. As a matter of fact, it does.

Gurney's correlation between activity orders and structural influences seems therefore to hold for the salts considered. This does not need to mean that the structural influences "cause" the activities to behave as they do, for it is just as plausible, in principle, to think that both "effects" are effects of some other cause (i.e., functions of a common set of independent variables). Gurney's postulate, however, states that the structural influences are indeed the "cause" of the activity effects, and he outlines a mechanism by which they may be imagined to operate. This is through overlapping of the structurally altered zones about the individual ions (which he calls the cospheres of the ions). This could modify the law of force operating between the ions, and so change the effective a, with significant consequences for the thermodynamic properties of the solution. A particularly interesting aspect of Gurney's explanation, if it is correct, is that it correlates quantities which are measured at (or refer to) infinite dilution with interactions which are meaningful only at finite concentrations.

Part Three

On the subject of ionic entropies, attention should be given to an advance in a different direction which is reported in two papers by Cobble (35, 36). These succeed in including oxygenated anions (35) and inorganic complex ions [e.g., FeF^{++} (36)] in the empirical framework created by Powell & Latimer (37) for describing the partial molal entropies of monatomic ions in aqueous solution. The equation of Powell and Latimer is

$$\overline{S}_i^\circ = 3/2R \ln M_i + 37 - 270Z_i/(r_i + x)^2 \qquad \text{III}$$

where $\overline{S}_i°$ is the conventional partial molal entropy (38) of an ion of kind i, in a standard state of hypothetical unit molality and referred to H^+ as zero, M_i is the atomic weight of the ion, Z_i (the absolute value of) its charge or valence, r_i its crystallographic radius in Å, and x a correction term equal to 1.00 Å for anions and 2.00 Å for cations. It describes with remarkable fidelity the broad outlines of the effects of M, Z, and r upon $\overline{S}°$, as shown by the way the straight line plot obtained from III when $\overline{S}_i° - 3/2\ R \ln M_i$ is plotted against $Z_i/(r_i+x)^2$ knifes through the not-very-wide spread of experimental points from Cs^+, ($r=1.69$, $\overline{S}°=+31.8$) and I^-, ($r=2.16$, $\overline{S}°=26.14$) to U^{++++}, ($r=0.89$, $\overline{S}°=-78$) and Pu^{++++}, ($r=0.86$, $\overline{S}°=-87$ e.u.). Some of the deviations from this line are, as mentioned by Powell and Latimer, presumably due to omission of a statistical term for the quantum weight or multiplicity, of such an ion as Fe^{+++}. Others may be due to uncertainty in the experimental values for the entropies. A systematic separation of $\overline{S}°$ values for anions and cations would also be produced if $\overline{S}°_{H^+}$ were not taken as equal to zero. In some cases, however, it seems reasonable to expect that there should be specific effects superposed on the general functional relationship which equation III represents. Gurney's discussion, quoted above, of the distances of closest approach of ions in solution seems to be relevant here. Applied to the closeness with which a water molecule can approach an ion it suggests that the different x corrections Powell and Latimer use for anions and cations may be expected to arise from differences in the laws of force both for attraction and repulsion when the water is differently oriented. So far, it simply restates Latimer's interpretation (39). It also suggests, however, that a difference in covalent contribution to the ion-water interaction, from whatever "par" contribution may be implied in the equation, may alter the law of force so as to make the "true" effective radius of an ion like Ag^+ differ from the one the formalism provides. Such effects could account for some deviations.

Of special interest is the apparent implication of the dependence of $\overline{S}_i$ on Z_i and r_i shown in equation III, that the loss of entropy on hydration may be proportional to the force of attraction exerted by a charge on a dipole rather than to the work required to charge a sphere in a dielectric medium (40). This law, proportionality to the first power of Z and inversely to the square of an effective radius, still holds in the slightly modified empirical equation (which omits M and uses altered coefficients and x values) presented by Powell (41). It seems clear that whatever detailed physical explanation of entropies of hydration is eventually hit upon, it will have to account for this kind of dependence on Z and r in the case of monatomic ions.

Cobble's extension (35, 36) of this kind of treatment to the more complex cases he treats is, of necessity, somewhat more involved. For the oxy-anions it consists in (*a*) changing the values of the empirical constants, and (*b*) substituting for the square of the corrected ionic radius the first power of the corrected distance of separation, r_{12}, of central atom from oxygen. The distance r_{12} is evaluated formally as the sum of the covalent radii of oxygen and

the central atom, and then corrected as described below. Cobble's equation thus becomes

$$\overline{S}_i^\circ = 3/2R \ln M_i + 66 - 81(Z_i/\rho) \qquad \text{IV}$$

where Z_i is again the ionic charge, $\rho = r_{12}/f$ and f is a correction factor, always somewhat less than unity, which is tabulated for the various geometrical forms (and, for tetrahedral form, for various charges) such ions may have. Thus, for singly and doubly charged tetrahedra (e.g., ClO_4^- and SO_4^{--}), $f = 0.74$; for PO_4^{---}, $f = 0.83$; for NO_3^-, $f = 0.68$. The reproduction of experimental data, from $Cr_2O_7^{--}$ ($\overline{S}^\circ = +32$) to PO_4^{---} ($\overline{S}^\circ = -68$ e.u.) is again gratifying.

For inorganic complex ions (36), the treatment likewise uses the first power of a corrected distance, as in equation IV but, once more, with altered constants. In this case, r_{12} is the internuclear distance from cation to ligand, (taken as the sum of ionic and/or covalent radii, as appropriate) and the factor f is unity when the ligand is a monatomic anion. When the ligand is NO, NH_3, CN^-, SO_3^{-2}, f is 0.65, but 1.0 again for hydroxyl complexes. More important, however, is that, in this case, a correction is required for the entropy gained by the water expelled from the hydration sphere of the cation. Cobble's formalism for this is to assume all cations as six-coordinated, and add 16.7 e.u. (the whole of the molal entropy of liquid water) to $\overline{S}_i^\circ$ of the complex for each water displaced by a ligand [cf. (42)]. The equation he arrives at is

$$\overline{S}^\circ = 49 - 99(Z/\rho) + nS^\circ(H_2O) \qquad \text{V}$$

where n = number of waters displaced, and $S^\circ(H_2O)$ is the molal entropy of water. This gives a line about which experimental points (themselves often not highly precise) for such ions as $Fe(NO)^{++}$, $Ni(NH_3)_6^{++}$, $CuCl_2^-$, $PdCl_4^{--}$, TiF_6^{--}, etc., scatter more widely than in the simpler cases, though they still lie in a clearly marked zone about it. For neutral "complex" species, such as $SnBr_3$, FeF_3, TlBr, TlCl, Cobble gives a separate equation,

$$\overline{S}^\circ = 132 - 354/r_{12} + nS^\circ(H_2O) \qquad \text{VI}$$

which gives good results (to 2 or 3 e.u.) for the eight species tested excepting $CdCl_2$ and AgCl, for which large deviations are found.

In a third paper, Cobble combines the methods outlined above with others related to entropies of formation and of hydration of nonpolar molecules, to obtain a formalism by which estimates can be made of standard partial molal entropies of ionic complexes (chelated and other) in which the ligand is a large organic molecule. Many of the considerations entering this treatment, however, lie outside the scope of the present discussion.

The question arises as to what the relationship may be between the Powell-Latimer-Cobble treatment of ionic entropies just outlined, and the structural concepts of Frank and Evans and of Gurney. The answer seems to lie in the fact that the former compares the ionic entropies only with each

other, and with the crystallographic radii and the chemical make-up of the ions, without inquiring why ions of such radii and make-up should have entropies as large or as small as those observed. That is to say, it calls attention to certain regularities which any theory must be in a position to account for before it can lay claim to completeness.

So far as the structural picture has now been worked out, it meets this test satisfactorily. That is, the structural picture gives a qualitative prediction of a rather strong dependence of the entropy of hydration of a monatomic ion on its charge and "size," and in the correct sense. Semi-quantitatively, also, it is in harmony with numbers of entropy units which lie in the range of those given by the empirical equations. Further than this it has not yet been elaborated. When a further elaboration is attempted it seems clear that the Powell-Latimer-Cobble equations will (*a*) probably offer valuable hints as to the best line to take, and (*b*) certainly provide important criteria of success or failure.

Even before this or some other explanatory theory has been fully worked out, however, the Powell-Latimer-Cobble equations have great practical utility in correlating known information, and in making possible the estimation of entropies (and, therefore, with heats, of reaction tendencies) of ionic species for which no data have as yet been obtained. Such estimates are used later in this chapter.

Part Four

An interesting experimental relationship between self-diffusion and activity coefficients was published during the year by Mills & Kennedy (43). They used the open-ended capillary method (44) to measure the self-diffusion of I^- in aqueous solutions of HI, LiI, KI, and RbI; in the last two cases measuring the cation self-diffusion also. Their measurements cover a concentration range from 0.01 to 0.06M at the lower end to 2M to 4M at the upper end. For K^+ in KI they find the same sort of maximum in the D–$c^{1/2}$ curve which Wang (45) and Wang & Miller (46) had found for Na^+ in KCl and in NaCl solutions, and had attributed to "distortion" of the water molecules immediately surrounding the ion. Such a maximum is not found for Rb^+ in RbI which, as Mills and Kennedy remark, is in conformity with Wang's conjecture regarding the relationship of this effect to cation hydration. They warn, however, against "speculation as to the cause of these maxima . . . until there is some explanation of their absence in all measurements so far reported by the diaphragm cell technique."

Noting that I^- diffuses (at any one concentration) progressively more slowly in the alkali iodides from LiI through RbI (using unpublished results of Wang for NaI), they note also that this is the order of activity coefficients of the salts in question. They plot $D\eta/\eta_0$ (self-diffusion coefficient of I^- corrected for viscosity changes) against the Debye-Hückel "First approximation" concentration function, $c^{1/2}/(1+0.3288\ \mathring{a}\ c^{1/2})$ using the $\mathring{a}$ values given by Harned & Owen [(15) parameter for Eq. 12-5-3] for these solutes.

With an over-all deviation of ± 2 per cent such a plot makes the points for LiI, HI, NaI, KI, and RbI fall on a single curve, only LiI seeming to show a (small) systematic deviation. Since the δ values were chosen to fit activity coefficient data, we have here a new and interesting evidence of the effectiveness of the same forces in the two kinds of phenomena. CsI was not measured but would presumably fall on the same curve. Since δ in CsI is less than the crystallographic radius sum, this would mean that whatever influence, short-range (association) or long-range (structure), makes the activity "too low," would also make the I^- diffuse "too slowly."

Mills and Kennedy perform another useful service in directing attention to the discrepancies between data on self-diffusion obtained by different experimental methods. A series of tests of various possible sources of error in their own open capillary method tends to confirm it as an accurate one when properly used, but they point out, correctly, that the question is not closed. It may be that this question is relevant to the issues raised by the next work to be reported.

This was published by Cuddeback, Koeller & Drickamer (47) and Cuddeback & Drickamer (48) who measured the self-diffusion of several ions in dilute aqueous solutions, under pressures from 1 to 10,000 atm., usually at a variety of temperatures from 0° to 75°C. These experiments require for their interpretation the results of earlier ones on the self-diffusion of CSS^{35} in CS_2 (49), of CSS^{35} in mixtures of CS_2 and other liquids [(50) several hydrocarbons and two alcohols], and of THO in water (47). In all cases, the diffusion coefficient was computed (51, 52) from the rate at which the scintillation intensity, produced in a cadmium tungstate plate, was found to build up as a result of progressive arrival of the soft β-radiation at the far side of a sintered glass plate initially full of inactive liquid. The quartz and sapphire windows through which the intensity was observed were of such aperture and thickness as to stand the pressures involved, and compression effects which determined the position of the "initial" diffusion boundary after pressure had been established were evaluated (49) from known compressibility data.

The change of diffusion coefficient D with pressure P was used to compute an activation volume, $\Delta V^{\ddagger}$ for the diffusion process, and also the change in this quantity with P. Temperature coefficients enabled a heat of activation, $\Delta H^{\ddagger}$, and its variation with P to be determined. An "absolute" entropy of activation, $\Delta S^{\ddagger}$ could not be obtained without making rather speculative assumptions about the detailed nature of the diffusion act, but $\Delta\Delta S^{\ddagger}$, the change in entropy of activation from its value at 1 atm., could be computed from the relative (to 1 atm.) values of D and $\Delta H^{\ddagger}$. The methods used in making these calculations are standard (53).

The results in the cases of CS_2 in non-hydrogen-bonded liquids always show, with one exception, a decrease in D with increase in pressure, but often following inflected curves and with curves of different shapes at different temperatures. Interpretation is given in terms of such concepts as diffusion

of CS_2 through a quasi-lattice of larger hydrocarbon molecules, and a difference in effect of pressure on the volumes in the normal and in the activated state, the latter difference driving the activation volume either up or down; sometimes first up and then down, or down and then up. These interpretations seem straightforward, and are usually supported by heat and entropy changes which fit well into a consistent picture. In the case of CS_2 in chlorobenzene, discontinuities and failure of reproducibility appear in the *D–P* curves, between 2000 and 3000 atm. These are attributed to a liquid-liquid transition in C_6H_5Cl which had also disturbed Bridgman's (54) *PVT* measurements.

Very different, as expected, are the results obtained for diffusion of THO in H_2O[(47) see Fig. 3]. Here at 0°C. and 25°C., the initial effect of pressure is

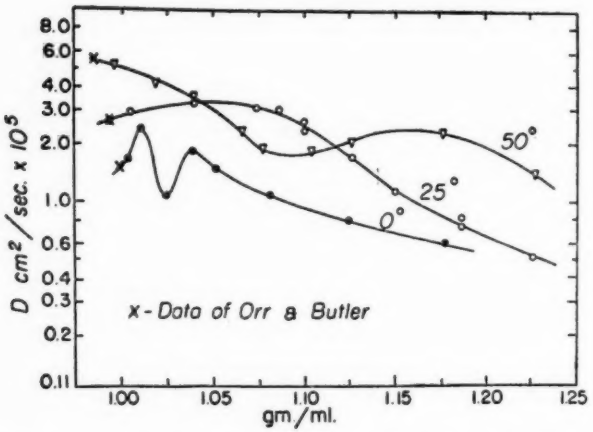

FIG. 3. Coefficient of self diffusion of THO in H_2O versus density. Reproduced by permission of H. G. Drickamer and the *Journal of Chemical Physics*.

to increase *D*, rapidly at 0° and slowly at 25°C. At 50°C. the initial effect is a slow decrease. This accords well with current beliefs about water structure and the effect of both rising temperature and increased pressure in breaking it down. In fact, the whole course of the 25°C. curve is about what would have been predicted, *D* turning down again at about 4000 atm. Less predictable are the findings that at 50° the initial decrease is followed by a minimum at about 3000 atm. and a maximum at about 6000 atm. Perhaps still less so are the two rather sharp maxima shown by the 0° curve at about 250 and 900 atm., respectively, with a narrow minimum between them at about 600 atm., and a smooth decrease above 1200 atm. These results could be explained if at 0°C., and perhaps at all temperatures, there were more than

two identifiable structural species of water [cf. Eucken (55)], with distinguishable equilibria between them, differently influenced by pressure.

When the diffusion of $H_2S^{35}O_4$ in 0.1N aqueous H_2SO_4 is measured (47), the results are qualitatively rather similar to those for THO with the difference that all the maxima in D are shifted to lower pressures, the first one at 0°C. being eliminated, resulting in an initial rapid decrease in D, by a factor of about 4, to 355 atm., followed by an almost equal increase to 840 atm.

When $S^{35}O_4^{--}$ is allowed to diffuse in 0.1N Na_2SO_4, 0.1N K_2SO_4, and 1N Na_2SO_4, further alterations are observed, some of which are shown in

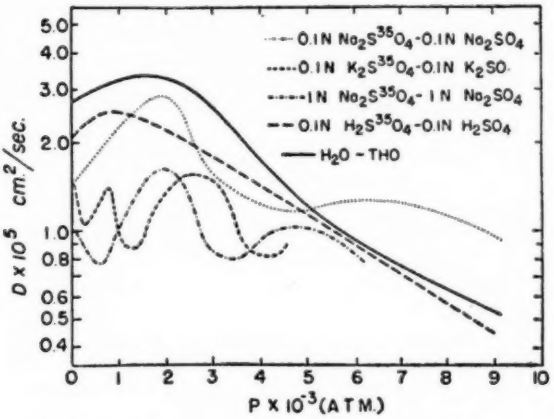

FIG. 4. Coefficient of self diffusion, at 25°C., of $S^{35}O_4^{--}$ in various solutions versus pressure. Reproduced by permission of H. G. Drickamer and the *Journal of Chemical Physics*.

Figure 4. The principal point for our present purpose is contained in the following quotation (p. 596):

> The similarity between water, 0.1N H_2SO_4 and 0.1N Na_2SO_4 is evident from Fig. 12 [our Fig. 4], but the 1N Na_2SO_4 and 0.1N K_2SO_4 have additional maxima and minima which are not easily explainable but which are definitely present.

The results (48) for Tl^{204} in 0.1N $TlNO_3$, Ca^{45} in 0.1 $Ca(NO_3)_2$ and 0.1N $CaCl_2$, and Hg^{203} in 0.1N $Hg(NO_3)_2$ are of the same general degree of complexity as in the sulfate cases and, comparatively, the $TlNO_3$ shows "additional maxima and minima."

There seems to be no doubt that, if these self-diffusion data are to be accepted as meaningful, structural ideas must be invoked at every turn in discussing them. The significance for "ordinary" electrolyte theory can per-

haps be pointed up by fastening attention upon the diffusion, at 25°C., of SO_4^{--} in 0.1*N* Na_2SO_4 and in 0.1*N* K_2SO_4 (Fig. 4). It is the sulfate which is being "observed" and presumably most of the diffusion in these solutions (0.1*N*) is accomplished by ions which are not members of associated pairs. Yet it matters significantly to the SO_4^{--} whether its counter ion is Na^+ or K^+, for examination of the figure reveals that whereas *D* starts up in Na_2SO_4 as *P* increases above 1 atm., in K_2SO_4 it starts down. This corresponds in the first case to a negative, and in the second to a positive $\Delta V^{\ddagger}$ or "activation volume," and appears to mean either that the data are unreliable or else that the SO_4^{--} ion "knows" at a distance the difference between Na^+ and K^+.

If this were true it would have several interesting corollaries. While it is not easy to predict the probable effect on the law of force between ions of the structural influences to which these diffusion anomalies are presumably to be ascribed, if would be surprising if they left the law of force entirely unchanged (cf. Gurney's hypothesis, reported above). If there were changes then, for example, differences from salt to salt in the Mayer *a* might arise from variations in the distribution of distances of separation which involved perturbation in the longer as well as in the shorter distances. Large *a* for Li^+ and Na^+ salts would then not need to be due to hydration, and small *a* for Cs^+ salts would not need to be due to association in any commonly accepted sense of these words. More serious is the possibility that if structural influences could produce "forces at a distance," the potential of average force between two rather widely separated ions might not only not be of simple coulombic form, but might not even be independent of the position of a third ion. In this case the postulate that *W* is a sum of pair potentials (equation I) might break down. This would make aqueous electrolytes inaccessible to many of the most promising modern statistical treatments.

In view of these considerations it would be of great interest to be able to estimate the probability that the results of Cuddeback, Koeller and Drickamer will be found to be in error in some respect that would bear on the theoretical issues they raise. A calibration error in the scale of *D* or of *P* would not suffice. On the other hand, peculiarities in the compressibilities of Na_2SO_4 and K_2SO_4 solutions might, if present but unknown, produce such effects as are here in question, for they would falsify the computed length of diffusion path. Such compressibility anomalies seem unlikely, in the light of Gibson's (56) experimental results. Neither does it seem likely that such differences as are discussed by Mills and Kennedy, between results obtained by different experimental methods, could do these peculiar things. Moreover, the fact that these salts, each in its own way, fit into the general pattern established by THO in ordinary water, and the further fact that the results with CS_2 in hydrocarbon mixtures show that the method is capable of giving civilized results when used on civilized materials, give the salt data a sort of weird plausibility and incline us to accept them, albeit tentatively and with crossed fingers.

Part Five

Wicke & Eigen (57) have given an unusually interesting new calculation of activity coefficients, heats of dilution and apparent molal heat capacities, in which they apply their recently proposed (10) [cf. also (58) and (59)] modification of the distribution law which forms the basis of the Debye-Hückel theory (3).

In this ingenious modification, the central idea is that the concept of a cloud of distributed charge may be introduced at the outset to provide a way, within the framework of the Debye-Hückel thought pattern, of taking into account the mutual steric influence referred to earlier in this review, of the "cloud" ions. This is done by postulating that an ion which occupies a volume v (thought of as including its hydration envelope) must displace a charge $v\rho$ (ρ = charge density), and that this displacement must make a contribution to the potential energy change when the ion is moved. At a distance r from a central ion one writes n^+_r and n^-_r for the average numbers of cations and anions per cm³. Then if ϵ^+ and ϵ^- are the absolute values of the ionic charges, $\rho_r = n^+_r\,\epsilon^+ - n^-_r\epsilon^-$. Again, since the occupancy of volume is one of the central features of the treatment, $N^+(\equiv 1/v^+)$, and $N^-(\equiv 1/v^-)$ are written as the numbers of possible "sites" per cm³ for cations and anions. If, for preliminary explorations, v^+ and v^- are taken equal, then $1/v = N^+ = N^- = N$, the total concentration of ion sites, and $N - n^+_r - n^-_r$ is the "concentration of vacant sites" at distance r.

The procedure, now, is first to write the Boltzmann distribution equation of the Debye-Hückel theory in differential form:

$$kT\, d\ln n^+_r + \epsilon^+ d\psi = 0 \qquad \text{VII}$$

for cations, and then to introduce the extra potential energy term for the displacement of distributed charge, getting

$$kT\, d\ln n^+_r + (\epsilon^+ - \rho_r v)d\psi = 0 \qquad \text{VIII}$$

ψ (r) being the potential as usual.

When the corresponding equation is written for anions (with appropriate sign changes), a little algebra involving ρ_r and N leads to a differential equation for cations which does not contain ρ_r, and which integrates directly to

$$\frac{n^+_r}{n^+}\,\frac{N - n^+ - n^-}{N - n^+_r - n^-_r} = \exp\left(-\epsilon^+\psi(r)/kT\right) \qquad \text{IX}$$

where the n's without subscripts are the stoichiometric concentrations (concentration at $r = \infty$) and the convention has been introduced that $\psi(\infty) = 0$. A corresponding equation holds for anions.

The second essential step in the treatment is less straightforward. It consists in arbitrarily modifying IX to provide that steric interference shall take place only between ions of like sign, obtaining

$$\frac{n^+_r}{n^+}\,\frac{N - n^+}{N - n^+_r} = \exp\left(-\epsilon^+\psi(r)/kT\right) \qquad \text{X}$$

and the corresponding expression for anions. Practically, or mathematically, this accomplishes two things. First, it makes possible the use of different hydration volumes, v^+ and v^- for cation and anion, leading to the possibility of different site numbers N^+ ($\equiv 1/v^+$) and N^- ($\equiv 1/v^-$). Second, it produces the desired result of giving a ratio ${n^+}_r/{n^-}_r$ which differs from the simple Debye-Hückel ratio to the first order in the expansion of the exponential. Equation IX, by reason of the symmetry with which cation and anion occur in the second factor of the left side, produces such a difference only in higher terms of the expansion. Wicke and Eigen justify the transition from IX to X by considering that the principal contribution to the exclusion volume v comes from hydration, and that the opposite orientation of the water molecules held by anions and by cations will permit extensive mutual penetration of their respective hydration spheres, reducing the extent to which cation and anion will "exclude" each other. This leaves only cation-cation and anion-anion exclusion. No claim is made that these assumptions are rigorously correct, but the formalism they lead to is useful, and is the one employed.

The use of the form X leads to a straightforward development for ρ, which, when introduced into the Poisson equation in the customary manner, yields a quantity κ', differing from the Debye-Hückel κ only in the presence of an extra factor $(1-n/\overline{N})^{1/2}$. Here

$$1/\overline{N} = \frac{\Sigma \nu_i Z_i}{\Sigma Z_i}\,\bar{v}$$

where Z_i and ν_i are the customary ion valences and ion numbers ($n_i = n\nu_i$) and $\bar{v} = 1/2\ (1/N^+ + 1/N^-)$ is the mean hydration volume of the two ion types. The computation of activity coefficients through the Debye charging process (60) and subsequent differentiation is complicated by the presence of the additional factor in κ' and the result for f_i is given by

$$\frac{\ln f_\pm}{\ln f_\pm{}^*} = \frac{\kappa}{\kappa'}\left(1 - \frac{2n}{\overline{N}}\right)\left[\frac{1}{1+a\kappa'} - 2Q\right] + 2Q\,\frac{\kappa'}{\kappa} \qquad \text{XI}$$

where

$$Q = \frac{\ln(1+a\kappa') - a\kappa' + (a\kappa')^2/2}{(a\kappa')^3}$$

and $\ln f_\pm{}^*$ is the limiting law value of $\ln f_\pm$. The a occurring in these expressions is the "distance of closest approach" as in the conventional Debye-Hückel "First Approximation." To relate it to $\bar{v}$, the "approximate relationship"

$$\bar{v} = (4/3)\pi a^3 \qquad \text{XII}$$

is employed, which reduces to one the number of empirical constants which must be specified in applying equation XI to the fitting of data.

Calculated values of $f_\pm$, using XI and XII and well-chosen values of a reproduce well the qualitative features previously referred to as character-

istic of the experimental values for the alkali halides. Wicke and Eigen direct particular attention to the way in which the minimum and subsequent rise above unity are provided for by their equation. They remark that for the a values which they use, ranging from 4 Å to 6 Å, corrections for the "higher terms" (12) in the expansion of the exponential never become significant, and conclude also that the three approximations they have introduced, namely, (*a*) the simplified form of the "vacant site factor" in X, (*b*) the relationship XII between $\bar{v}$ and a, and (*c*) the use throughout of the dielectric constant of pure water, seem to be permissible to comparatively high concentrations. In earlier publications (61, 62) they have considered concentrations high enough to require a concentration dependence of $\bar{v}$ because of competition of ions for hydrate water. This factor does not enter, however, in the work here under discussion.

In applying the foregoing treatment to calculations which are to be compared with experimental activity coefficients of specific salts, Wicke and Eigen introduce the additional postulate of incomplete dissociation, which they use, among other purposes which it serves, to reconcile the low value of a otherwise required to fit XI to the data, say, for CsCl (2.5 Å) with the high value a must have for all salts on the basis of the hydration theory of Eucken (32) and Eigen & Wicke (63). Before turning to this, however, we may remark that the significance of equation XI, and of the treatment leading to it, seems to be different on different levels of discussion. Qualitatively, and as an aid in the intuitive understanding of the kind of connection which should exist between the physics of hydration and the mathematics of activity coefficients, it marks an important advance over the Debye-Hückel theory. So far as concerns rigor, however, and even mathematical self-consistency, it is less successful. Onsager, for example, has pointed out (64) that the Güntelberg charging process (65) should lead to the same expression for $\ln f_{\pm}$ as does the Debye charging process (60), and has taken the fact that the two methods give different results when applied to the "higher terms" calculation (12) to be a mark of the lack of self-consistency of the "higher terms" formalism. The simple Debye-Hückel "First Approximation" formalism, on the other hand, is self-consistent in this respect; the two charging processes, when applied to it, do give identical results. When the Wicke-Eigen treatment is subjected to this test, a gross discrepancy appears, and the expression obtained by using the Güntelberg charging process is not capable of predicting a rise of $\ln f_{\pm}$ above zero. For the purposes of this theory, therefore, as in the Gronwall-LaMer-Sandved development, one is forced to use the Debye charging process.

Physically, also, it seems that the concept of mutual free interpenetration of hydration shells of anion and cation is rather awkward in a system like aqueous LiCl (see below) where a is taken as 6 Å, and K_c, the dissociation constant, is taken equal to ∞, for $K_c = \infty$ means a zero probability that the hydration shells will be penetrated. On the other hand, there is a qualitative reason that Wicke and Eigen do not mention for not including anion-cation

exclusion in their "correction" of the Debye-Hückel model. This lies in the fact that the Debye-Hückel "First Approximation" already contains, in the parameter a, a way of accounting for such exclusion. Ions of unlike sign, in this representation, will usually bear to each other the relation central ion-cloud ion. Ions of like sign will usually bear to each other the relation cloud ion-cloud ion. Volume exclusion in the first relationship is taken care of by the Debye-Hückel a. Therefore, the correction should limit itself to volume exclusion in the second relationship. This involves (to a certain approximation) only like-signed ions, and is therefore more appropriately represented by X than by IX, and X leads to XI. It therefore appears that the Wicke and Eigen treatment may be classed with the Gronwall-LaMer-Sandved treatment (12) in that each tells us something which is qualitatively valuable but not mathematically exact.

In view of the success Stokes & Robinson (66) had in introducing the idea of hydration into numerical calculations of $\ln f_{\pm}$ for alkali halide salts through the use of the Bjerrum correction (19), it is of interest to inquire why such a correction should not also be used by Wicke and Eigen. As mentioned in the discussion of the Mayer theory, hydration can, in principle, affect $\ln f_{\pm}$ in two ways: through weakening of electrostatic interaction due to the less close approach of the charged particles, and through removal of water from its solvent function. Such removal, however, which is what the Bjerrum correction accounts for, is logically the same as making certain regions of configuration space inaccessible, and is therefore taken care of by a distribution function which is realistic with respect to such inaccessibility. Thus Eigen and Wicke, with a qualitatively realistic distribution function, could not use a Bjerrum correction. Moreover, their treatment, which in this respect resembles Mayer's, is logically preferable to the use of a Debye-Hückel distribution, in which a takes care of only a portion of the inaccessibility, plus a supplementary correction to take care of the rest.

This advantage is illustrated by the observation that if the mathematical form of equation XI is applied to salts with large but unhydrated ions, it predicts for such solutes also that $f_{\pm}$ will rise above unity, in agreement with what Mayer's theory has taught us to expect. In making such an application it would be possible to use any of a number of assumptions regarding the relation between a and $\bar{v}$. The relation of equation XII, which Wicke and Eigen use for this purpose, is peculiar in making a a radius in the cloud-cloud exclusion, whereas it is a diameter in the cloud-central ion relationship. Its "real" meaning seems thus to be that of an average of two numbers, one of which is an effective radius and the other an effective diameter. The success of this apparent overemphasis on cloud-cloud exclusion may reflect a kind of compensation for the overdrastic simplification by which equation X completely ignores anion-cation exclusion in the cloud. Even the compensation implied by XII seems somewhat inadequate, however, since the data for LiCl require an a value of 6 Å if XI is to fit them (see below), whereas in the Mayer theory an a of 4.35 Å suffices for this salt.

As stated above, Wicke and Eigen, in developing the foregoing formalism for numerical application, combine it with the assumption of incomplete dissociation. They introduce this assumption with great ingenuity to produce the additional results of accounting for experimental values of $\Phi(L)$, apparent molal heat content, and of the concentration dependent part, which we shall call $\Phi(J)$, of the apparent molal heat capacity. To each (I-I or II-II) salt they assign a value of K_c, the dissociation constant, defined by

$$K_c = \frac{\alpha^2}{(1-\alpha)} f_{\pm a}^2 c \qquad \text{XIII}$$

where α = degree of dissociation, and $f_{\pm a}$ is $f_\pm$ from XI, corrected to "true" ionic concentration. Straightforward thermodynamics then leads to

$$\ln f = \ln (\alpha f^+_a) \qquad \text{XIV}$$

from which numerical values can be obtained by a process of successive approximation. Equation XIV contains (implicitly) two disposable constants a and K_c, and good agreement with data (67) is obtained for LiCl with $a=6$, $K_c=\infty$; for NaCl with $a=5$, $K_c=6$; for KBr with $a=5$, $K_c=2.5$ and for CsBr with $a=5$, $K_c=0.9$. These comparisons cover the concentration range 0 to 2.0 moles/liter.

Turning now to heats of dilution, treatment of XI by standard methods yields an expression for the electrostatic-and-exclusion part of $\Phi(L)$. In this case, however, a new quantity, $d \ln \overline{N}/d \ln T (\equiv N')$, appears in the formula, and an estimate must be made of its value. For LiCl, in which the influences represented in equation XI are assumed to account for the whole of $\Phi(L)$, it is found that experimental data can be fitted by taking N' constant with concentration, and equal to 1.5. Values of N' of 1.0, 1.5, and 2.0 are therefore used for the other salts, without discussion.

Equation XII would lead us to expect that $d \ln a/d \ln T = \frac{1}{3}N'$, but Wicke and Eigen reject this implication, on the ground that a, being an anion-cation distance, should be less temperature-dependent than $\bar{v}$, which measures mutual exclusion of ions of like sign. Their formalism therefore explicitly assumes $da/dT = 0$, thereby suppressing an otherwise non-negligible term in $\Phi(L)$, and giving a temperature dependence to the weighting of the terms in the averaging process implied in XII.

This calculation makes the electrostatic-and-exclusion part of $\Phi(L)$ positive for all c, and some additional cause is needed to account for the turning down of $\Phi(L)$ at higher c values displayed by many salts. The appropriate explanation of the framework here constructed is to postulate an absorption of heat by the dissociation produced by making the solution more dilute (68). The knowledge of K_c obtained from fitting activity data permits prediction of the amount of dissociation which will accompany the dilution process and thus of the amount of heat absorbed. The molal heat of dissociation for the reaction

$$MX(aq) = M^+(aq) + X^-(aq) \quad \Delta H = D_\infty \qquad \text{XV}$$

is therefore the only other disposable constant, and, again after straightforward thermodynamics, an expression for $\Phi(L)$ is obtained in terms of a, K_c, N', and D_∞. This is found to fit the data (67) very nicely for LiCl, for example, with $a=6$, $K_c=\infty$, $D_\infty=0$; for NaCl with $a=5$, $K_c=6$, $D_\infty=4.4$, and for KBr with $a=5$, $K_c=2.5$ and $D_\infty=3.0$ kcal./mole.

A further result can be obtained by use of the thermodynamic relationship between D_∞ and the temperature coefficient of K_c, for this means that once D_∞ and K_c have been chosen for one temperature the effect of change of temperature upon α should be calculable, and this should give a contribution to $\Phi(J)$, the concentration-dependent part of $\overline{C}_{p2}$. Unfortunately, $\Phi(J)$ will also contain the contribution that comes from electrostatic-and-exclusion effects, and this, from differentiation of XI, contains not only N' but also $d^2\overline{N}/dT^2$. Concerning this latter quantity very little can be conjectured, and Wicke and Eigen make the formal assumption that it is zero, justifying this by the statement that the term in which $d^2\overline{N}/dT^2$ occurs is, in any case, very small. With this assumption, and using the values of a, N', K_c, and D_∞ previously accepted, they obtain spectacular agreement between observed and calculated values of $\Phi(J)$ for NaCl, KCl, and LiCl. Of particular interest is the fact that this calculation reproduces the characteristic simple form of $\Phi(J)$, which is approximately linear in $c^{1/2}$ up to high concentrations for all I-I salts. As Wicke and Eigen note, no previous theoretical explanation has been advanced for the striking difference between this simple form for $\Phi(J)$ and the more complicated forms of $\ln f_\pm$ and $\Phi(L)$.

Several features of this group of calculations make it impressive. One is the versatility of the model, on which apparently straightforward treatments can give equations of the right forms to fit so wide a variety of data. Another is the fact that since the same three disposable constants (a, K_c, D_∞) are used to fit three different types of curve for three different experimental quantities for any one salt, the arbitrariness in choice of constants has been greatly reduced, if not eliminated. Against this, it must be admitted that for each type of calculation there has been at least one simplifying assumption, of which the only real justification is the empirical fit it makes possible. Moreover, there is another test that can be applied, and the results it gives are less encouraging. This is to use K_c and D_∞ to calculate ΔS° for the reaction XV, using the relation

$$\Delta S^\circ = \Delta H/T + R \ln K_c. \qquad \text{XVI}$$

The units employed in XV and XIII give ΔS° in conventional units, referred to the conventional standard states of hypothetical molal solutions of all species. Inserting the Wicke and Eigen values of K_c and D_∞ gives $\Delta S^\circ = +18.3$ for NaCl; $+11.9$ for KBr; and $+11.5$ e.u. for CsCl. For comparison we have the following experimental values from the literature: -6 e.u. for

AgCl (69); −4.4 e.u. for TlCl; and −0.3 e.u. for TlBr (70). The latter agree in general with the expectation that extinction of charge in aqueous solutions should increase entropy, and that dissociation, which increases free charge, should lower entropy. From this point of view, the ΔS° values given by Wicke and Eigen's constants are seen to be of the wrong sign.

It is possible, of course, that for dissociation of a neutral molecule into singly charged ions the gain in entropy arising from the increase in number of particles might, in some cases, outweigh the loss due to the influence of the charges on the water. In fact, when the Powell-Latimer and Cobble equations III and VI are combined to give an expression for ΔS° of reaction XV in terms of ionic radii, the estimates this gives for the entropy of dissociation of alkali halide pairs are (13) sometimes positive and sometimes negative. For the cases of immediate interest they are: NaCl, $\Delta S^\circ = 8.1$; KBr, $\Delta S^\circ = 2.0$; and CsCl, $\Delta S^\circ = -2.4$ e.u. While two of these are indeed positive, and while no great accuracy can be claimed for them, it is seen that each of them lacks some 10 e.u. of being positive enough to match the value obtained from the Wicke-Eigen constants. All in all, therefore, we incline to the opinion that the latter are to be rejected, at least until further evidence is brought forward to support them. To put our objection into other language, if the alkali halides had such large heats of dissociation as those quoted, they would have no business being as highly dissociated as they are claimed to be [cf. AgCl: $D_\infty = 2.7$ kcal./mole, $K_c = 5 \times 10^{-4}$ (69)].

"Rejecting" numbers obtained for ΔS° of reaction XV means, of course, expressing the opinion that the parameters K_c and D_∞ have more complicated meanings than the simple ones which Wicke and Eigen assign to them. This is entirely equivalent to what we did in saying that the Mayer-Poirier a for CsI was not a true distance of closest approach, but reflected also some nonmodel effects. In the present case, the implication is that something is taking place in these solutions over and above the effects Wicke and Eigen have considered. One such possibility, in the light of our previous discussion, is that $\Phi(L)$ contains a contribution arising from a concentration-dependent shift in the water structure equilibrium. If so, then the "true" D_∞ would be different from the one here obtained. Depending on the form of the concentration-dependence of the new effect, K_c might also need to be changed, which, in turn, would call for modification of a and, possibly, of some of the formal assumptions. Another consequence would be that $\Phi(J)$ would likewise have a contribution from the same cause.

As to the possibility of occurrence of a structural term in $\Phi(L)$, Frank & Robinson (71) have discussed structural influences as affecting $\overline{S}_1 - \overline{S}_1^\circ$, a quantity to which $\overline{L}_1$, and therefore $\Phi(L)$, is closely allied. Their discussion can be improved in the light of the later work of Frank and Evans and of Gurney which makes it appear that a part of the concentration dependence of the entropy of dilution can be described in terms of the progressive overlap, as concentration increases, of the regions of structural alteration about the separate ions.

A corresponding effect can also be predicted from the standpoint of Eucken's theory (32, 55) of water structure and its alteration by ionic solutes. Eucken postulates [rather implausibly, it seems to us, and in marked departure from other modern trends; cf. (25, 31, 72, 73)] that water is an ideal solution made up of four species, H_2O, $(H_2O)_2$, $(H_2O)_4$, and $(H_2O)_8$, the mole fractions of which are governed by chemical equilibria, with equilibrium constants, heats, etc. for which he gives numerical values. When ions are dissolved in the water they are pictured as "removing" water molecules by a kind of adsorption, and this, with the dilution produced by the presence of the new species, causes a series of shifts in the polymerization equilibria. Eucken's expression for such a shift leads to the conclusion that addition of solute affects the mole fractions of the different polymers differently. It turns out that because the polymers also differ from each other in their heat contents (per mole of H_2O) the progressive shifts in equilibria as salt is added will produce a contribution to $\overline{L}_2$, the heat of transfer of a mole of salt from infinite dilution to a solution of molality m.

Possible objections to Eucken's model, or to that of Frank and Evans and of Gurney, would not weaken the point of this discussion, which is that any attempt to consider the effect of ions on water structure seems likely to predict a concentration-dependent influence on the thermodynamic properties of the solution.

One further point should be made in the discussion of the Wicke-Eigen theory (pp. 61–68). Their distribution function differs from that of Debye & Hückel only in an alteration of electrostatic influences, namely, a weakening of the electrostatic interaction of ions occasioned by their less close approach. This weakening should, in principle, never be able to convert the net electrostatic effect into a repulsion; neither should it contain within itself the non-electrostatic influence of excluded volume. The question then arises why the Wicke-Eigen equation does, in fact, predict an upturn in the curve of $\ln f_{\pm}$ versus c. It appears that the answer is simply that the distribution function (X) was selected because it has this effect. The treatment imitates, so to speak, the results of the Mayer theory in which a realistic distribution function, one taking into account both electrostatic and volume-exclusion effects, is correctly converted into an activity coefficient.

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SOLUTIONS OF NONELECTROLYTES[1]

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Introduction.—Scientific workers whose interests touch upon the properties of nonelectrolyte solutions gave, during the year 1953, much attention to both theoretical and experimental descriptions of these systems. An event of great moment in the reporting and evaluating of such work was the One Hundredth General Discussion of the Faraday Society on "The Equilibrium Properties of Solutions of Non-Electrolytes" (1). In the Spiers Memorial Lecture, Hildebrand (2) described results of some past and present experiments having particular bearing on the structure of solutions. Among the topics are quasi-crystalline theory and some of its limitations, clustering and the properties of solutions under conditions of critical mixing, the definition of "regular" solutions, intermolecular forces and their representation, and acid-base interactions and molecular complex formation.

Guggenheim (3), introducing the theoretical part of the Discussion, reviewed recent trends in theoretical work and pointed out the importance of the molecular interchange energy w in determining the properties of mixtures. Of special interest is the fact that useful approximations for the free energy of mixing as a function of composition and interchange energy consist of the sum of terms corresponding to $w=0$ (configurational terms) and terms proportional to w (interaction terms). Such approximations correspond to neglect of deviations from randomness. The nonzero nature of the temperature coefficient of w is of interest since it appears directly in formulas for the entropy and internal energy of mixing in the above approximations. Everett (4), introducing the discussion of experiments reported at the Faraday Society meeting, described development of techniques for studying equilibrium solution properties. He emphasized the desirability of furnishing experimental information in a form suitable for comparison with theory and pointed out the critical role of gas imperfection studies in the elucidation of solution properties. Other reports from the Faraday Society meeting are noted in the appropriate sections in the remainder of this review.

General.—Scott (5) described a number of models currently used to approximate solutions and presented a critical comparison of the model properties.

During 1953 considerable attention was given to the problem of orientation effects in mixtures. Pople (6) presented a general method for relating thermodynamic properties of solutions to an intermolecular potential describing directional forces. He expanded the intermolecular energy u_{st} associated with a molecule of species s and a molecule of species t in terms of

[1] The survey of the literature pertaining to this review was completed in January, 1954.

normalized surface harmonics. For orientation forces represented by interaction of permanent electrostatic moments, the expansion coefficients are easily expressed in terms of the moments. Application to liquid solutions centers around perturbation treatment of $u_{st}-u_{oo}$, where u_{oo} is a reference substance energy which stems from the operation of central forces. Treating the noncentral terms as small compared with the central term and keeping only the leading terms in the expansion of the partition function, one obtains the excess Helmholtz free energy of mixing at constant volume in terms of the pair distribution function for the reference substance and the above energy expansion coefficients. Pople studied a simple lattice distribution for pairs of molecules and concluded that, in general, the excess entropy of mixing for orientation constributions should be approximately equal to the excess Helmholtz free energy of mixing divided by the absolute temperature.

Tompa (7) investigated the properties of a lattice model with intermolecular energies dependent on mutual orientation. His treatment, based on the combinatory method of the strictly regular solution, assumes a molecular interaction energy dependent on orientation for the specific case of a mixture of spherical molecules and molecules with symmetry $D_{\infty h}$. The result is an expression for the excess free energy of mixing as a function of composition and interaction energies. For plane, square, and simple cubic lattices with uniform interaction energy for either all like pairs or all unlike pairs, explicit numerical results are obtained. Curves for excess functions plotted against mole fraction exhibit typical asymmetry. The excess entropy of mixing for a system with uniform interaction energy for all unlike pairs and with like pair energies dependent on orientation has an "S" shape like that experimentally found for methanol solutions. Tompa observed that contributions to the excess thermodynamic functions can come from sources other than orientation effects and did not characterize the deviations of any experimental system in terms of the parameters of his equations.

Orientation effects in solutions received both experimental and theoretical attention from Barker and his co-workers. Barker, Brown & Smith (8) investigated vapor-liquid equilibria in the ethanol—carbon tetrachloride system at 45°C. and 65°C. and calculated the thermodynamic properties of the mixture from their results. The excess free energy of mixing they represented by an expression of the type $x_1x_2[a_0+a_1(x_1-x_2)+a_2(x_1-x_2)^2+a_3(x_1-x_2)^3]$. To explain the deviations from ideality, they used a lattice model and determined interactions in hydrogen bond formation and in alcohol-solvent contacts so as to give agreement of theory and experiment for the equimolar mixture. They then found reasonable agreement for all compositions. The interactions so found do not, however, reproduce satisfactorily the properties of another system, methanol—carbon tetrachloride.

Interest in the lattice theory of solutions and in the hydrogen bond led Barker (9) to investigate orientation effects using the quasi-chemical lattice and the Kikuchi modified lattice (10). The free energy is minimized subject to the restrictions imposed by the structure of the lattice. The results are

expressed in the form of simultaneous equations of high degree; numerical values of the excess free energy are obtained, in the limiting case of very large negative interaction energy, for pairs of molecules in the quasi-chemical approximation and for a triangular lattice model in both the quasi-chemical approximation and Kikuchi approximations. There is qualitative agreement between the pair results and the Kikuchi triangle results, which latter values Barker believes to be fairly close to the correct ones. He concludes that the quasi-chemical pairs approximation is satisfactory so long as the lattice is not close-packed. Barker (11) examined the quasi-chemical approximation in the theory of strictly regular mixtures and succeeded in proving the method formally convergent. In addition, he demonstrated that direct extension of the pair approximation to larger groups with an arbitrary lattice reproduces the results of Kikuchi's treatment (10). The lower approximations appear to be in error since they cause inconsistencies in the values of the free energy. Both lower and higher approximations are in error by producing nonzero positive or negative values for the derivative of the free energy with respect to configuration variable at the point of separation into pure components.

Bell (12) made a statistical study of regular ternary solutions with particular emphasis on phase separation and equilibria in cases for which the free energy is symmetrical in two or three of the components. He developed a double tangent method for binodal curves in the phase diagram and applied it in the location of triple points. The equilibrium equations apply to binary solutions in which one component is dipolar with two possible orientation states.

Rowlinson (13) examined the smoothed potential model of Prigogine & Mathot's (14) cell model and the Lennard-Jones-Devonshire model of solutions and compared the corresponding theories of pure liquids with experiment. Calculating for the comparison the quantity RT less the latent heat of vaporization, he found that the Lennard-Jones-Devonshire model with first, second, and third neighbor interactions perhaps can be an adequate basis for a solution theory, but that great practical difficulties of numerical integration present themselves in the treatment of this model.

Considerable attention was given to the theory of mixtures of monomers and r-mers, an r-mer being defined as a molecule occupying r quasi-lattice sites. Rushbrooke, Scoins & Wakefield (15) used the quasi-crystalline model of athermal liquid mixtures to calculate the vapor pressure of monomer—r-mer solutions as a power series in the volume concentration of r-mer. The expansion coefficients are analogues of the irreducible integrals of Mayer's (16) real gas theory. Simple approximations for the coefficients lead to the Flory and the Miller-Guggenheim vapor pressure equations for monomer—r-mer mixtures. For values of r above two, the vapor pressures depend slightly on the flexibility of the r-mer. Guggenheim (17) discussed general relations between solution properties and cluster integrals and showed that expressions for the properties of athermal mixtures in terms of Mayer's

cluster integrals reduce to those for ideal mixtures when the solute and solvent molecules are of identical size. Prigogine, Trappeniers & Mathot (18) extended the cell model of liquids to open-chain unbunched molecules. Internal degrees of freedom of molecules are but slightly altered by solution; translations, rotations, and twisting modes are assumed to be reduced to vibrations with low frequencies determined by the interatomic forces. The average force is estimated from a Lennard-Jones potential, with the lattice theory used to estimate the number of nearest neighbors. This treatment is extended to solutions of monomers and r-mers, and the excess functions are calculated. The contributions of the combinatory or order-disorder factors are also taken into account, following earlier work of Guggenheim (19). Calculations are made for a mixture of carbon monoxide as monomer and propane as dimer. It appears that contributions of the combinatory factor and the effects of the force fields are of comparable importance in determining the excess entropy. The excess volume curve has been obtained for a monomer-dimer combination and has much the same form as the experimental curves for the systems dibenzyl—benzene, diphenyl—benzene, and toluene—benzene, although an exact comparison of the actual values cannot be made since some of the parameters are not known.

Longuet-Higgins (20) used classical statistical mechanics to investigate the thermodynamic properties of chain molecule solutions and found that the free energy of mixing at constant temperature and pressure must have the form $kT\Sigma_i N_i \ln\phi_i$ where ϕ_i is the volume fraction. He showed that the useful equation for the free energy of mixing $(\Delta G)_{T,p} = kT(N_a \ln\phi_a + N_b \ln\phi_b) - Ed_{ab}\phi_a\phi_b$ (where E is the intermolecular energy and d_{ab} is a constant defined in terms of the interaction potentials of different kinds of segment) can be obtained without recourse to the restrictive assumptions of lattice theory and with only the assumptions that the molecules have sufficient length and that the relative positions of the ends of two separate chains are independent of the length of the molecules. He obtained the following generalization of Brønsted's (21) congruence principle: two mixtures will have the same solvent properties and equations of state if each contains chain molecules which can be divided into identical sets of fragments by cutting the chain in suitable places. Results given by Koefoed (22) confirm this generalization experimentally by showing that solvent properties of a mixture of chain species depend only on the average chain length in the medium.

Prigogine & Bellemans (23) extended the cell model of solutions to apply to mixtures of spherical molecules of slightly different radii. They followed the previous program of Prigogine (14) by using a smoothed potential model and obtained expressions for the excess thermodynamic properties in terms of purely molecular data. For mixtures of molecules of the same size but different force fields, the theory predicts, in the case of dispersion forces, a negative excess volume, and, for mixtures of molecules of different sizes and the same force fields, it predicts expansion on mixing. For solutions in which the largest molecule has the strongest field, there is usually an expansion on

mixing. Mathot & Desmyter (24) measured total vapor pressures and volume changes on mixing for binary mixtures of tetramethylmethane with benzene, cyclohexane, and carbon tetrachloride as well as volume changes on mixing for binary mixtures of carbon tetrachloride with several chloro- and hydroxy-substituted tetramethylmethanes. The theory of Prigogine and Bellemans successfully predicts the signs of excess free energies and volumes of the systems considered.

Saroléa (25) investigated the error introduced in the cell model by the assumption of random mixing. The nonrandomness corrections are effects of higher order than those due to volume variation and thus are negligible in many cases. Nasielski (26) used the cell theory of Prigogine & Mathot (14) to determine the activity coefficients, heat of dilution, and entropy of dilution for a binary solution with molecules of like size. In this theory the excess chemical potential is the sum of a term in $(1-x)^2$, where x is the mole fraction of the component considered, and two terms related to the volume change on mixing. Pople (27) employed the cell theory of liquid mixtures without restricting the cell potential to that of a harmonic oscillator or flat-bottomed well. Even when second order terms are included, the theory does not account quantitatively for the excess entropy of mixing or for the composition asymmetry of excess functions; it does predict the proper signs for excess properties.

Saroléa-Mathot (28) developed a statistical theory of associated solutions, taking account of the evolution of heat on association and the decrease in the number of possible orientations of the associated molecules. The excess thermodynamic properties were obtained from spectroscopic values of association constants for solute-solvent complexing and good agreement with experiments on acetone-chloroform solutions was obtained. The theory was also used to treat hydrogen bonding in alcohol solutions. Comparison of theory and experiment for methyl alcohol—carbon tetrachloride mixtures indicated that the theory is satisfactory for simple molecules with hydrogen bonding. Huet, Philippe & Bono (29) measured the vapor pressures and infrared optical densities of ethanol—carbon disulfide and ethanol—dioxane solutions. They calculated the activity coefficient ratio f_a/f_b, where a refers to unassociated molecules and b refers to the solvent. Prigogine, Mathot & Desmyter (30) showed that f_a/f_b is equal to c, the fraction of solute molecules unassociated, if solution nonideality stems from complexing alone. The values of c obtained from infrared measurements are considerably greater than f_a/f_b for the carbon disulfide solution and smaller than f_a/f_b for the dioxane mixture.

Zimm (31) derived, for a binary mixture, an equation connecting the chemical potential, compressibility, and a single cluster integral. McKay (32) set up, in form especially suitable for integration, differential equations relating activities of the components of ternary solutions.

Buckingham (33) derived a general expression for the dielectric constant of liquid mixtures with ellipsoidal molecules. The treatment is most suitable

for strongly polar solutes in solvents with small dielectric constants. Buckingham tested these results with existing values and found that the calculation succeeds for important cases such as aqueous solutions of glycine and alanine, for example.

Thermodynamic properties.—Campbell & Hickman (34) studied vapor-liquid equilibrium for stannic chloride—octane and stannic chloride—tetrachloromethane systems. The latter materials, with nearly identical cohesive energy densities, conform to Raoult's law within experimental error. Properties of the former system are reasonably well described by Hildebrand's regular solution theory as are the critical solution temperatures for perfluoroheptane in stannic chloride, in tetrachloromethane, and in octane which Campbell & Hickman also determined.

Cantoni & Feldman (35) obtained activity coefficients from measured liquid and vapor equilibrium compositions of nitromethane—nitroethane mixtures. The system is not sufficiently nonideal to exhibit azeotrope formation. Ballard & Van Winkle (36) studied vapor-liquid equilibrium for 2-propanol with methyl propyl ketone and with methyl isobutyl ketone and calculated activity coefficients for the mixtures. Schumacher (37), studying the boiling points of oxygen—ozone mixtures, found large deviations from ideality, as shown by azeotrope formation at −105.3°C. and by the existence of partial miscibility with a critical temperature of −180°C. Metzger & Disteldorf (38) determined the vapor pressures at 90°C. and boiling points at 750 mm. for thiazole—water solutions. They found the van Laar equation, $\log \gamma_2 = B(1 + Bx_2/Ax_1)^{-2}$, with A and B disposable parameters, a very good representation of the large positive deviations from ideality. Rose *et al.* (39) proposed a numerical method for evaluating from experimental data the properties of binary liquid mixtures which obey the van Laar or Margules equations.

Rutledge, Jarry & Davis (40) measured the freezing points of uranium hexafluoride—hydrogen fluoride mixtures from −85°C. to 105°C. They found a miscibility gap extending from 10 to 80 formula per cent uranium hexafluoride. Below 61.2°C., the temperature at which the miscibility gap begins, the solubilities are much lower than the ideal value, a fact which reflects the large difference in cohesive energy densities of the components. There is no evidence of compound formation. Jarry *et al.* (41) obtained, in the form of activity coefficients, quantitative expression for the nonideality by studying vapor-liquid equilibrium over the entire composition range and over the temperature range 40° to 105°C.

Clark & Din (42) studied the vapor pressures and compositions of ethane—ethylene mixtures saturated with solid carbon dioxide and of the binary solutions of these three components. The ethylene—ethane system exhibits very slight positive deviations from Raoult's law. The solubility of carbon dioxide in ethylene indicates small positive deviations from ideality, whereas the deviations for carbon dioxide—ethane solutions are positive and large. The latter system has been discussed by Charnley *et al.* (43). The nitrous

oxide—carbon dioxide system was found by Cook (44) to obey the conformal solution theory of Longuet-Higgins (45) in the critical region.

Mitchell & Wynne-Jones (46) examined existing data for the systems hydrogen peroxide—water and ethanol—water in an effort to understand the contribution of strong hydrogen bonding to solution nonideality. They noted that addition of hydrogen peroxide depressed the temperature of maximum density and that the phenomenon of maximum density is not observed for peroxide mole fractions above 0.015. In the alcohol solution the temperature of maximum density first increases and then decreases with addition of alcohol. The two systems differ qualitatively in their thermodynamic properties in that, although both have negative excess entropies of mixing and negative heats of mixing, the peroxide system has negative deviations from Raoult's law and the alcohol system has positive deviations. Mitchell and Wynne-Jones suggested that the above facts reflect ability of peroxide molecules and the inability of ethanol molecules to enter and fit in a water structure; the alkyl group presumably prevents a fit for ethanol despite strong hydrogen bond formation. This conclusion is reinforced by studies on the acidity of the systems.

Glew & Moelwyn-Hughes (47) studied very dilute solutions of methyl halides in water and obtained values of pressures and compositions for vapor-liquid equilibrium and of the heat of solution of both gaseous and liquid halides in water. From their pressure-solubility measurements, they found the interaction energies, E, in the van Laar expression $P_2/P_2^0 = x_2 \exp(x_1^2 E/kT)$, where P_2 is the vapor pressure of dissolved component 2, P_2^0 is the vapor pressure of pure component 2, and the x's are mole fractions. In spite of the variation in E from compound to compound, the temperature coefficient of E is given by $59.555 - 0.15776T$ for all the methyl halides, so that E is a maximum at 377.5°K.

Good *et al.* (48) measured the solubility of *p*-terphenyl in *o*-terphenyl, in *m*-terphenyl, and in biphenyl. Their results showed that the ratio of solubility in *o*- and in *m*-terphenyl is given as $RT \ln(x_{ac}/x_{ab}) = V_a[(\delta_a - \delta_b)^2\phi_b^2 - (\delta_a - \delta_c)\phi_c^2]$ where a refers to *p*-terphenyl, ϕ_i is the volume fraction and δ_i is the solubility parameter. Ratio of solubility in biphenyl and in *o*-terphenyl and ratio of solubility in biphenyl and in *m*-terphenyl are given satisfactorily by the above expression increased on the right by the lattice theory terms

$$T\left\{\left(1-\frac{m_a}{m_b}\right)\psi_b - \left(1-\frac{m_a}{m_b}\right)\psi_c + \frac{2}{zq_a}\left[\left(1-\frac{m_a}{m_b}\right)^2\psi_b^2 - \left(1-\frac{m_a}{m_c}\right)^2\psi_c^2\right]\right\}$$

in which zq_a is the number of lattice sites adjacent to the sites occupied by the m_a segments of molecule a and ψ_i is the site fraction.

Staveley, Hart & Tupman (49) determined constant pressure heat capacity, coefficient of thermal expansion, and adiabatic compressibility of the following binary mixtures, selected to be widely representative: benzene with ethylene dichloride, with carbon tetrachloride, and with acetic acid; acetone with carbon disulfide and with chloroform; ethyl alcohol with carbon

tetrachloride and with water. The different measured properties were combined to produce constant volume heat capacities. The authors characterized the mixtures in terms of ΔC_v defined as $C_v - x_1 C_{v1} - x_2 C_{v2}$. ΔC_v reflects the nonideality of a given system and the temperature coefficient reflects in some degree the interactions producing nonideality.

Critical phenomena.—Mayer (50) has given a review of theories of the critical state, and has reported experiments by Sinclair (51) who found that in the triethylamine—water system the composition of the vapor phase (and hence the fugacity of each component) was independent of composition over an appreciable range of concentrations in the homogeneous solution region as much as three or four degrees below the lower critical solution temperature, thus being in accord with the ideas of McMillan & Mayer (52). These results do not seem to be in agreement with vapor pressure measurements of Kohler (53). Rowden & Rice (54) have given the details of their measurements of the cyclohexane—aniline system, which they believe shows no such region of constant fugacity in the one-phase region, but which they believe has a coexistence curve with a flat, horizontal top. Criticisms by Zimm (55) concerning the latter point have been answered, at least in part. Atack & Rice (56) have now made measurements of the densities ρ_1 and ρ_2 of the coexisting phases, and of the homogeneous phase above the critical temperature T_c. Taking the appearance of a dense fog as determining T_c, as Rowden and Rice had done, they found $\rho_2 - \rho_1$ proportional to $(T - T_c)^{0.34}$; however, there was a sudden change in the density of the upper layer of the liquid, occurring within a range of 0.001 to 0.002°, about 0.005° below the temperature of appearance of dense fog. They took this as evidence that the critical temperature was a little lower than had been supposed and interpreted the sudden change of density as a separation of phases when the flat top had been reached. They also measured the interfacial tension and showed that it tends to zero at the critical temperature, but were unable to determine whether the slope of the interfacial tension-temperature curve tends to zero. The effects of small quantities of water on the critical temperature were explained as being due to a negative adsorption of a reasonable order of magnitude. In the case of the liquid-vapor equilibrium in a one-component system, recent work of Whiteway & Mason (57) and Weinberger, Habgood & Schneider (58) indicate that the flat top of the coexistence curve is largely, perhaps entirely, due to the gravitational compression effect.

Jura *et al.* (59) have measured the specific heat (C_p) of critical mixtures of water and triethylamine and of perfluoroheptane and *iso*-octane and have found that this has a marked maximum at the critical temperature. In the latter case they have also measured the specific volume and have found that the coefficient of expansion has a maximum at the critical temperature. These two effects go together, the mixing occurring with expansion and absorption of heat. C_p for a solution is roughly analogous to C_v for a liquid-vapor system; in the latter case, Michels & Strijland (60) have found a similar effect in carbon dioxide. Amirkhanov & Gurvich (61), however, failed to

find any maximum in the specific heat of phenol—water solutions in the critical region. They attribute the finding of such effects by earlier Russian workers (62) to failure of the latter to stir their solutions. Amirkhanov and Gurvich find that large temperature gradients can arise in the critical region, which they attribute to poor convection resulting from the high viscosity in this region. However, Jura *et al.* state that in their case "stirring was adequate to insure equilibrium."

Much consideration has been given to the conditions reponsible for upper critical solution points (UCSP) and lower critical solution points (LCSP) in binary liquid solutions. Previously worked out conditions (63) for critical points can be expressed in terms of the excess functions G_e (free energy), H_e (enthalpy), and S_e (entropy): for a UCSP we have $\partial^2 G_e/\partial x_2^2 = -RT/x_1x_2$, $\partial^2 H_e/\partial x_2^2 < 0$ and $\partial^2 S_e/\partial x_2^2 < R/x_1x_2$, while for an LCSP we have $\partial^2 G_e/\partial x_2^2 = -RT/x_1x_2$, $\partial^2 H_e/\partial x_2^2 > 0$ and $\partial^2 S_e/\partial x_2^2 > R/x_1x_2$ where x_1 and x_2 are mole fractions of the components. Using this result, and assuming that G_e, H_e, and S_e have the same sign throughout the range of concentrations, and no inflection points, it can be shown [see Prigogine (64) and Copp & Everett (65)] that at a LCSP the conditions $H_e < 0$ and $S_e < 0$ must hold and at a UCSP we must have $H_e > 0$. It should be stated that these assumptions have been criticized by Haase (66), and Korvezee (67); the discussion, however, proceeds on the assumption that $H_e < 0$ and $S_e < 0$ at an LCSP and $H_e > 0$ at a UCSP. In order to have a closed solubility loop, then, the excess specific heat, $C_{p,e}$, must be positive. Copp and Everett [see also Copp (68)] have given a detailed graphical discussion of the conditions for the various kinds of critical points. They have presented measurements on four binary mixtures containing amines and have considered the properties of a number of other systems in the light of these criteria, which they believe to give a qualitative understanding of the properties of these systems. They stress the importance of some type of association, with the simultaneous effect on heat and entropy of an "inert" hydrocarbon grouping, in causing an LCSP in binary solutions containing water. These same factors have also been stressed by Prigogine (64) and Bellemans (69) who have developed a cell theory of the thermodynamic properties of solutions. They showed that a system of spherically symmetrical molecules could not show an LCSP; some kind of association phenomenon is necessary, but, as also shown by Haase (66) by a simple modernization of an old argument of Washburn (70), a perfect solution of molecules in various stages of association cannot separate into phases; other kinds of imperfection must also be present. Andon, Cox & Herington (71) have obtained from vapor pressure measurements the thermodynamic properties of dilute solutions of pyridine bases in water. They found that, in general, the greater the activity in dilute solution the smaller the range of miscibility of the pyridine base with water, the least miscible being those with most methyl groups, as found by Andon & Cox (72). The correlation of activity in dilute solution is, of course, related to the G_e curves, as was pointed out by Copp & Everett (73) with an interesting analysis and

correlation of the data on a number of solutions of hydrocarbons, acetates, *n*-aliphatic alcohols and acids, pyridines, and aliphatic amines with water. The thermodynamics of solutions showing consolute points was further discussed upon the basis of a commonly used specific form of G_e (=constant times x_1x_2) by Guggenheim (74) and by Copp & Everett (65); Herington (75) suggested that this form would not occur in real systems showing a large miscibility gap. Rice (76) discussed the criterion for an LCSP on the basis of entropy of transfer of a constituent between solutions of different composition and showed on this basis that association of some kind would be necessary. Timmermans & Lewin (77) presented some new experimental data and discussed the trends in various binary systems, some of which show complete miscibility, but with indications, such as critical opalescence or very flat vapor-pressure curves (small dependence of vapor pressure on concentration over a range of concentrations), that they are almost ready to separate into two phases. These could theoretically be made to separate out by placing them under a negative pressure; this has not succeeded experimentally, but addition of small amounts of a third component can often cause separation to occur. Timmermans (78) has shown that substitution of deuterium oxide for water also has a tendency to cause separation to occur and this has recently been confirmed by Cox (79). Barker & Fock (80) worked out the statistical thermodynamics of a number of lattice models, designed to show the effects of anisotropic forces on the solubility curve. A model in which an active group on each species of molecule interacts strongly with the other molecule showed a closed solubility loop. Other models, including one which was supposed to represent hydrogen bonding, showed no LCSP. The authors suggest that compound formation alone is not sufficient to give an LCSP. Brusset & Bono (81) have given a systematic discussion of binary systems showing a UCSP.

Scott (82) has noted the often-remarked similarity between critical points and λ-transitions. He argues that the cubic coexistence curve for the vapor-liquid equilibrium suggested by Guggenheim (83) would imply that C_v should be infinite at the critical point (though this does not seem to be a thermodynamic necessity). By analogy he argues that the specific heat at the λ-point should also be infinite, and he plots data for ammonium chloride and silicon dioxide which indicate that the specific heat behaves as though it were becoming infinite more rapidly than would be predicted by his equations.

Furth (84) has reported measurements of Chow Quantie on the critical scattering of light by the mixtures aniline—cyclohexane (I) and isobutyric acid—water (II), and has analyzed the results in terms of correlation of densities. In II, correlations out to about 700 Å are indicated at the critical point; in I, the correlation extends to about 1400 Å, and there is a region of negative correlation extending from about 900 to 1400 Å.

Sette (85) discusses binary solutions which show a maximum in ultrasonic absorption at a certain concentration. This is due to structure of some

kind in the mixture. In the neighborhood of a critical point (e.g., in the nitrobenzene—*n*-hexane solution) there is a sharp maximum in the absorption, associated with formation of clusters of nonaverage composition. These clusters cause an increase in viscosity; also the equilibria involved have a wide range of relaxation times. Both these effects might contribute to ultrasonic absorption over a wide range of frequencies. The situation has also been discussed by Alfrey & Schneider (86) who made measurements of ultrasonic absorption on the triethylamine—water and nitrobenzene—*n*-hexane systems in the critical region. They find that the sound attenuation is too great to be accounted for as classical viscosity attenuation (the same situation holds even well away from the critical point), and it does not behave properly for scattering attenuation. The conclusion is that the attenuation has to do with a relaxation phenomenon involving clusters. Similar conclusions had been reached earlier by Chynoweth & Schneider (87), who measured dispersion as well as attenuation in the critical region.

Benzene solutions.—Meares (88) measured the heats and volume changes on mixing ethylbenzene with ten aromatic hydrocarbons and four dialkyl phthalates. The systems ethylbenzene—benzene and ethylbenzene—*p*-cymene were studied over a range of compositions. The heat of mixing is small for the hydrocarbon solutions but is large for the phthalates. For the *p*-cymene case, the heat of mixing at constant volume is symmetrical with respect to the volume fraction. The heat of mixing at constant volume for the benzene—ethylbenzene mixture is symmetrical with respect to the volume fraction for concentrations between 1 and 0.6 volume fraction ethylbenzene but for other concentrations varies as $f_1 f_2^2$, where f_1 and f_2 are the volume fractions of benzene and ethylbenzene, respectively.

The heat of mixing of benzene—diphenyl solutions was found by Kortüm, Dreesen & Freier (89) to be symmetrical in the mole fraction. They calculated the entropy of mixing and tested the theory of athermal mixtures, suggesting that the unexplained temperature dependence of the entropy of mixing could arise from orientation effects in the pure liquids and from high temperature discontinuities of the liquid lattice. Korvezee, Ruiter & Stuyts (90) examined experimentally the heat of mixing benzene with ethylene dichloride. Their results are represented very well by $x(1-x)[A+B(2x-1)+C(2x-1)^2]$, where x is the mole fraction and A, B, and C are functions of the temperature. Their analysis demonstrates the value of plotting the ratio of the heat of mixing to $x(1-x)$ against $2x-1$. Schäfer & Wolff (91) obtained values of the heat of mixing acetone with saturated hydrocarbons by observing the increment in the carbon-oxygen valence vibration at 1708 cm.$^{-1}$ in the Raman effect.

Allen & Caldin (92) measured the boiling points of benzene solutions of benzoic, *p*-toluic, anisic, *m*-iodobenzoic, *o*-chlorobenzoic, and phenylpropiolic acids; from their results they calculated the standard thermodynamic functions for acid dimerization. They suggested that the partial offsetting of association entropy loss by entropy gain arising from the freeing of previously

oriented solvent molecules provides a qualitative explanation of the fact that changes of entropy on dimerization of carboxylic acids are smaller in liquid solution than in the gas phase. Davies & Griffiths (93) measured the solubility of a series of dicarboxylic acids in benzene over the range 30° to 65°C. The temperature dependence of the solubility seems to indicate rather large deviations from ideality. Eerbeek's theory (94) is not borne out by the experimental solubilities.

Le Fèvre and co-workers (95, 96) measured the dipole moments of furan, thiophene, and pyrrole in the gaseous state and in benzene solution and found, for the ratio of solution moment to gas moment, in the case of thiophene, quantitative agreement between experiment and the theory of Buckingham & Le Fèvre (97). Qualitative agreement exists for furan and pyrrole.

Iodine complexes.—Studies of iodine complexes in 1953 have dealt with special properties. Kortüm & Walz (98) measured the electric moments of iodine complexes by measuring the dielectric constant of cyclohexane solutions of iodine with benzene, naphthalene, diphenyl, dioxane, and pyridine. The dissociation constants of the complexes were found by measuring the solubility of iodine in the solutions, following the method of Kortüm & Kortüm-Seiler (99). The constants decreased in the order in which the compounds are written in the above list, the dissociation of the pyridine complex not being observable at all. From these measurements all the necessary concentrations were known, and the contributions of the unassociated parts to the dielectric constant could be found from measurements on binary solutions in cyclohexane. The electric moments found were large; for example, about 3 Debye units for the dioxane complex. This is in agreement with the idea of an electron transfer from dioxane to iodine, which, in view of the large moment, may occur to a greater extent in the ground state than was visualized by Mulliken in his theory (100). Kortüm & Wilski (101) have measured electrical conductivity of solutions of iodine in pyridine. The conductivity increased rapidly with time, which was attributed to a chemical reaction. The initial conductivity, however, behaved as a function of concentration, like the conductivity of a weak electrolyte, and the dissociation constant, presumably of the reaction

$$Py \cdot I_2 = Py \cdot I^+ + I^-$$

was measured.

Extensive measurements of the infrared spectra of iodine solutions in a variety of solvents have been briefly reported by Glusker, Thompson & Mulliken (102). It is believed that these results can be interpreted in terms of the electron-donor-and-acceptor theory noted above. When pyridine is the solvent, the changes in the spectrum upon addition of iodine are greater than in the other cases, and it is believed an ionic molecule or ions, as in the above chemical equation, may be formed. A similar conclusion was reached by Kleinberg *et al.* (103), who attributed subsequent changes in the spectrum to chemical reaction. A complex series of chemical reactions apparently

takes place when iodine is dissolved in quinoline.

Diffusion coefficients of iodine in organic solvents at 25°C. have been measured by Stokes, Dunlop & Hall (104). The product of diffusion constant and solvent viscosity had the following values for various solvents: hexane, 1.29; heptane, 1.35; carbon tetrachloride 1.38; dioxane, 1.30; benzene, 1.29; toluene, 1.19; *m*-xylene, 1.11; mesitylene, 1.01 (dynes $\times 10^{-7}$). The low values in the last three cases were interpreted as arising from complex formation; an appreciable fraction of the iodine is tied up effectively as part of a larger molecule, hence diffuses more slowly. Iodine also forms complexes with benzene and dioxane, but the effect in these cases is apparently not sufficient to show up.

He^3-He^4 solutions.—Vapor-liquid equilibrium in isotopic helium solutions and the experimental results of Sommers (105) were examined by Morrow (106), both to obtain activity coefficients and to measure the success of a real solution model previously employed (107) in treatment of the solution λ-point shift. Excess chemical potentials are given satisfactorily by expressions of the type $\mu_1^e = Bf_2^2$, where f_2 is the volume fraction of one of the components. The fact that the measurements are limited to dilute solutions of He^3 prevents direct use of Sommers' results to elucidate the temperature dependence of normal fluid heat capacity or of other normal fluid properties below the λ-point. Determination of the experimental activities of the isotopic components makes possible a clear distinction between the predictions of current two-fluid theories of the λ-point shift as shown by Morrow (108). The λ-point shifts obtained by King & Fairbank (109) from their second sound experiments are of little aid in the judging of relative merits of theories, since there is a very great discrepancy between their results and the predicted values of all existing theories. Sommers and co-workers measured (110) the heat of mixing of He^3 in He^4 for a dilute solution and found heat to be absorbed; combining this result with previously measured vapor pressures, they calculated the entropy of mixing and found it to be about 10 per cent lower than the ideal value. On Taconis' theory (111), one would expect absorption of heat, since addition of He^3 causes some He^4 to change from superfluid to normal fluid. Confinement of He^3 to normal fluid would mean lowering of entropy, counteracted by increase of entropy when superfluid is transformed into normal fluid. Quantitative calculations of these entropy effects are perhaps possible.

Band & Nelson (112) obtained from the cluster theory of saturated vapors expressions for the vapor pressure of isotopic helium solutions and employed an empirically adjusted nonlinear interpolation formula to relate the mixture cluster surface energy functions to those of the pure gases. The results appear to indicate anomalously low concentrations of the lighter isotope in the cluster surfaces.

Prigogine & Philippot (113) used the cell theory of solutions to examine the nonideality of He^3—He^4 solutions. Their results indicate that the mass difference of the isotopes, and thus the zero point energy, rather than the

statistics, is the most important source of deviations from ideality. For the equimolar mixture, the estimated energy of mixing is of the order of one or two calories per mole.

Gaseous solutions.—Gorski & Miller (114) used the method of Edwards & Roseveare (115) to study the volume change on mixing at constant pressure and temperature for carbon dioxide—nitrogen solutions, oxygen—nitrogen solutions, and carbon dioxide—oxygen solutions. From their results, they calculated the second virial coefficient combination $2B_{12}-B_{11}-B_{22}$ which, when combined with literature values of B_{11} and B_{22}, yields the mixture coefficient B_{12}. In the case of the nitrogen solutions, they found satisfactory agreement between these coefficient values and those calculated from the transport pair potentials and statistical mechanics and suggested that lack of agreement for the carbon dioxide—oxygen solutions stems from inadequacy of the combination rules used to calculate the energy term in the statistical mechanical integral expression for B_{12}. They did not study empirical combination schemes for obtaining B_{12} from B_{11} and B_{22}. Michels & Boerboom (116) measured the volume change on mixing at constant pressure for a large number of gaseous solutions, including helium—argon mixtures and all binary combinations of hydrogen, nitrogen, carbon dioxide, and carbon monoxide. Using the expression $\Delta(PV)/PV=x_1x_2(2B_{12}-B_{11}-B_{22})$ and experimental values of $\Delta(PV)/PV$, B_{11}, and B_{22}, they calculated B_{12} and used it to find the corresponding Lennard-Jones parameter ϵ_{12}, for σ_{12} assumed to be $0.5(\sigma_{11}+\sigma_{22})[1+(7\alpha_1/16\sigma_{11}^3)(\mu_2^4/\sigma_{22}^6\epsilon_{11}\epsilon_{22})^{1/2}]^{-1/6}$. This ϵ_{12} is given very nearly by the geometric mean of ϵ_{11} and ϵ_{22} for nitrogen—hydrogen, nitrogen—carbon dioxide, and nitrogen—carbon monoxide mixtures.

Flood (117) studied equilibrium of water between vapor and solid sodium bromide dihydrate in order to determine the validity of the Gibbs-Dalton law for gaseous water solutions at low pressures. Assuming that the added gases do not alter the chemical potential of water in the crystals, he found that mixtures of water with hydrogen, with helium, and with argon deviate from the Gibbs-Dalton law only 0.3 per cent for pressures up to 100 mm.

Lambert (118) studied the second virial coefficient for polar gases and gaseous solutions and interpreted deviation from the law of corresponding states as the result of association made possible by dipole interaction or hydrogen bonding. The coefficient B_{12}, defined as $(B—x_1^2B_{11}—x_2^2B_{22})/2x_1x_2$ where x's are mole fractions, B_{11} and B_{22} refer to pure gases, and B is the coefficient for the mixture, can be written as sum of a corresponding states contribution and an association contribution, which latter is given as $-RT/K_p$. K_p is the mass action constant of the dimer. Calculation of K_p from the above relations with experimental coefficients at different temperatures leads to an apparent heat of association surprisingly close to the value found for liquid mixture in the case of ether—chloroform solutions.

Solutions of gases in liquids.—Acetylene conforms closely to Henry's law in aqueous solution, as shown by Vestin & Löfman (119); in acetone solution, as shown by Hölemann & Hasselmann (120), for pressures below 10 atm. and temperatures above 25°C., it conforms reasonably well to Henry's

law, but is more soluble at higher pressures than one would expect from Henry's law.

Gjaldbaek (121) tested the applicability of the equation

$$\mu_2^M = RT[\ln \phi_2 + (1 - V_2/V_1)\phi_1] + V_2\phi_1^2(\delta_1 - \delta_2)^2,$$

μ^M being the chemical potential change on mixing, to solutions of carbon dioxide in the solvents perfluoro-*n*-heptane, heptane, cyclohexane, carbon tetrachloride, benzene, and carbon disulfide and found that the approximate expression $\mu_2^M = RT[\ln x_2 + V_2(\delta_1 - \delta_2)^2]$ gives better results. The solubility parameter 4.1 calculated for carbon dioxide he replaced by the empirical value 5.1 in order to get a reasonable fit. The abnormally large solubility in benzene suggests complex formation, perhaps as in iodine solutions.

Burrows & Preece (122) examined the solubility of helium in Apiezon oil and in silicones between 20° and 80°C. and found that a plot of $\ln [L(T/s)^{1/(n+1)}]$ against s/T was linear; L is the Ostwald solubility coefficient and s is the surface tension. This relationship was obtained from consideration of the solubility process in terms of cavity formation in the solvent followed by filling of the cavity with gas molecules. Use of a cavity formation energy expressed by $4\pi r^2(s - \mathrm{d}s/\mathrm{d}\ln T)$ gives

$$\ln [L(T/s)^{1/(n+1)}] = (n + 1)^{-1}R^{-1}[4\pi r^2 N(n + 1) + E_a/s][s/T] + A$$

where E_a is the energy liberated when gas enters the cavity, N is Avogadro's number, r is the solute radius, and A is a constant of integration.

Reamer, Sage & Lacey (123) measured the molal volumes of *n*-pentane—hydrogen sulfide mixtures over a large range of temperatures, pressures, and compositions; Reamer *et al.* (124) made a similar study of decane—hydrogen sulfide solutions.

Webster (125) studied an empirical correlation between solubility of gases in liquids and increase in vapor pressure of the liquids in the solutions over that of the pure liquids. Webster believes that the critical factor in determining the vapor pressure increment is the formation of a gaseous solution containing molecules which would otherwise condense.

Solutions of solids in gases.—Diepen and co-workers (126) measured the solubility of aromatic compounds in ethylene in the critical region; their study included the ternary system ethylene—naphthalene—hexachloroethane. They measured (127) the solubility of naphthalene in supercritical ethylene over a large range of temperatures and pressures. Ewald, Jepson & Rowlinson (128) obtained theoretical expressions for the solubility of solids in gases by representing the chemical potentials of gaseous components in terms of a virial expansion. Keeping only terms in the first and second powers of the density, they found

$$\ln (x_2/x_2^0) = (V_2^s - 2B_{12})V^{-1} + (V_2^sB_{11} - 3C_{112}/2)V^{-2}$$

where x_2 is the mole fraction of component 2 in the gas, x_2^0 is the mole fraction component 2 would have if its concentration in the mixture were that of the pure saturated vapor, V_2^s is the molar volume of solid component 2, V is that of the gas, and the B's and C_{112} are virial coefficients. For comparison with experiment they calculated the virial coefficients from a 6–12 Lennard-Jones potential with energy and collision diameter parameters

obtained from the critical volume and critical temperature. Calculation and experiment agree very well for the simple system carbon dioxide—air; there is only qualitative agreement for more complicated systems such as *p*-chloroiodobenzene—ethylene, which has been investigated experimentally by Ewald (129).

Robin & Vodar (130) continued their work on solubility in compressed gases, testing their equation $\ln(m/m_0) = (\rho/22.4)(V_s - 2B_{ab}N)$, where m is the volume concentration of solute in gaseous solution, m_0 is the mass of solute per unit volume without foreign gas, ρ is the density, V_s is the molal volume of solute, N is Avogadro's number, and

$$B_{ab} = \int_0^\infty [1 - \exp(-\epsilon_{ab}/kT)]\, 4\pi r^2 dr$$

with ϵ_{ab}, the Lennard-Jones potential. They obtained good agreement with experiments on such systems as iodine in carbon dioxide and methanol in methane.

Metallic solutions.—Bridgman (131) studied bismuth—tin solutions over a wide range of pressures and compositions and discovered a new phase corresponding to BiSn. Oriani investigated the thermodynamic properties of iron—nickel (132) and of cobalt—platinum (133) solutions. The former system, studied by a gas equilibration method, exhibits only slight deviation from ideality and nearly random distribution for solutions with low nickel content. Properties of the latter system, calculated from electromotive force values of the cell $Co(s)/Co^{++}/Co—Pt(s)$, include heat absorbed on mixing rather than heat evolved as assumed in the quasi-chemical theory of short range order. Oriani suggested that the theory falls short because it omits vibrational contributions to the entropy and strain energy contributions to the heat of solution.

Sundén (134) determined the standard electrode potentials of cells of the type $Hg/Hg_2Cl_2/NaCl(m=0.1)//In(ClO_4)_3/In—Hg$ with amalgam concentrations from 0 to 100 per cent indium. He described the deviation of liquid amalgams from ideality in terms of concentrations of compounds with the general formula $InHg_n$. The advantages of this method of analyzing the deviations are not clear in this instance. Spicer & Banick (135) determined the solubility of indium in mercury between 10° and 156°C. and found solid solution formation. Keck & Broder (136) used the temperature dependence of the solubility of silicon and germanium in gallium and indium to find the heats of solution. From measured electromotive force values for cells of the type $Zn(l)$ or $Zn(s)/ZnCl_2$ in $KCl—LiCl(l)/Zn—In(l)$, Svirbely & Selis (137) found large positive deviations from ideality in Zn—In alloys; the system exhibits a positive heat of mixing.

Scatchard & Westlund (138) calculated the thermodynamic properties of solid α-silver—zinc solutions from measurements of the vapor pressure of zinc in the mixtures. They found a remarkably large nonideal entropy of mixing. The excess entropy of mixing is much larger than that of α-brass and is about twice that of nickel-gold alloys.

Thurmond (139) studied existing measurements of the solubility of germanium and silicon in Group III, IV, and V elements and obtained an equation for the liquidus temperature as a function of the atom fraction of

germanium, the heat of fusion, and the temperature of fusion. Thurmond & Struthers (140) found that the solid solubility of antimony and of copper in germanium, and of copper in silicon pass through maxima as temperature increases. Riccoboni, Genta & Fiorani (141) determined activity coefficients of Cd—Cu liquid alloys from electromotive force of the cell Cd(l)/KCl—LiCl—$CdCl_2$(l)/Cd—Cu(l). Bever & Ticknor (142) compared the heat of solution of cold-worked and of unworked gold-silver alloys in tin to find the energy stored on working. The results suggest an approach to a maximum of stored energy as the strain increases. Hardy (143) found that the expression $A_1x^2(1-x)+A_2x(1-x)^2$ represents the excess free energy of mixing for the systems silver—copper, silver—platinum, aluminum—zinc, and gold—platinum.

No attempt has been made to review work on order-disorder phenomena in general, but mention may be made of the papers presented in Paris, June, 1952 (144), and of a review of the Ising lattice by Newell & Montroll (145).

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ISOTOPES[1]

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Introduction

This review covers some of the 1953 publications dealing with the enrichment and analysis of isotopes, with their abundances and natural variations, and with their properties and applications in rate processes and equilibrium systems. Isotope work in structure, atomic spectra, and mass measurements is also considered. In the omission of much interesting work consideration has had to be given to the length of the review, the setting of a reasonable limit to the domain of physical chemistry, and the avoiding of excessive duplication of other reviews in this volume.

Isotope Enrichment and Analysis

Enrichment.—In 1949 Clusius (1) suggested that the separation of multicomponent isotope mixtures in a hot wire column could be improved by the addition of auxiliary gases. Such gases of appropriate mass and collision cross section concentrate along the column at positions intermediate between those of the isotopes of interest and may be separated from the latter in another step, perhaps chemical. The principle is applicable to other types of separation processes. In 1953 Schumacher (2) included the effect of auxiliary gas addition in a theoretical treatment of the separation of multicomponent mixtures in the thermal diffusion column. Clusius & Schumacher (3) used suitable mixtures of isotopic hydrogen chlorides to facilitate separation of the argon isotopes. The distribution of species along the column is

light end A^{36} HCl^{35} DCl^{35} A^{38} HCl^{37} DCl^{37} A^{40} heavy end.

They obtained A^{36} containing 0.6 per cent A^{38} and A^{38} of 90 per cent isotopic purity, compared to natural abundances: A^{36}, 0.337 per cent; A^{38}, 0.063 per cent; and A^{40}, 99.600 per cent. Auxiliary gases for other systems were suggested.

David (4) discussed the theory of continuously operated Clusius-Dickel columns.

Faltings & Seehofer (5) described germanium isotope enrichment in a gas centrifuge. They observed separation factors exceeding theoretical values and discuss this behavior at some length.

The electromagnetic enrichment of stable isotopes in the Oak Ridge calutrons was reviewed by Keim (6). Enrichment of 177 stable isotopes in 43 elements has been achieved. Bernas (7) described the electromagnetic separator

[1] The literature survey for this review was concluded in December, 1953. Some of the later issues of foreign journals were unavailable.

of the French atomic energy group. Danish and Dutch electromagnetic separators have previously been described by Koch (8) and by Kistemaker & Zilverschoon (9).

Rupp & Binford (10) discussed methods of irradiation and processing in radioactive isotope production at Oak Ridge.

The enrichment of He^3 from liquid He^3-He^4 solutions is of theoretical and practical interest. Soller, Fairbank & Crowell (11) described a separation method for processing 2 liters of liquid helium per hour and raising the He^3 atom fraction from 1.5×10^{-7} to 5×10^{-3}, corresponding to a separation factor of 3×10^4. Their separation depended on the heat flush phenomenon of Lane *et al.* (12): if heat and refrigeration are applied at opposite ends of a vessel containing liquid He below the λ-point, the He^3 flows with the normal component of He^4 toward the cold end of the vessel. Atkins *et al.* (13) reported raising the concentration of He^3 from 2 per cent to 64 per cent in a single step, utilizing the more rapid flow of liquid He^4 through a small leak and the enrichment of He^3 in the vapor over the residual liquid. Enrichment by flow should cease when the He^3 concentration becomes high enough to bring the solution to its λ-point for the operating temperature, i.e., when all superfluid He^4 is converted to normal component. Pure He^3 can be prepared from the decay of tritium, which may be produced by the reaction Li^6 (n, α) H^3.

Zelikoff, Aschenbrand & Wyckoff (14) described a photochemical enrichment of Hg^{202}. In a similar research, Billings, Hitchcock & Zelikoff (15) used the radiation from a cooled Hg^{198} lamp to cause selective reaction of excited Hg^{198} with water vapor (nitrogen carrier). The Hg^{198} content in the HgO was 15 per cent compared to the 10 per cent natural abundance. Previously, McDonald & Gunning (16), using a hot Hg^{198} lamp and dried air, had found a depletion in the Hg^{198} content of the HgO. They attributed this result to a broadening and self-reversal of the exciting radiation.

Analysis.—The commonest method of isotope analysis is the mass spectrometer. There is an increasing use of simultaneous collection for high precision. Under favorable conditions peak ratios are obtained with a precision of 1–2 parts in 10^4, about a factor 10 better than with good single beam collection. Wanless & Thode (17) described conversion of a conventional instrument to simultaneous collection. Inghram & Chupka (18) described a multiple filament ionization source for analysis of solids. Stevens & Inghram (19) described a ratio recording system suitable for this type of source and electron multiplier detection. Isotopic lead analysis using lead tetramethyl was discussed by Collins, Russell & Farquahar (20) and by Ducheylard, Lazard & Roth (21). Farquahar, Palmer & Aitken (22) found good agreement between this method and one involving distillation of solid $PbCl_2$ or PbI_2 into the ion source. Keim (6) listed the compounds used by Oak Ridge for mass spectrometric analysis of enriched isotopes. Precise deuterium analysis of natural water, involving conversion to hydrogen gas and simultaneous collection at masses 2 and 3 was described by Friedman (23). Washburn, Berry

& Hall (24) described direct introduction of D_2O into the spectrometer. Suppression of a spurious mass 19 peak, probably H_3O^+, was discussed. Memory effects are still serious, and comparison with standard samples is desirable. A proper method of sample introduction into the ion source is important.

Kluyver & Milatz (25) reported improvement of an infrared analyzer so that the C^{13} in a 30 mg. CO_2 sample can be determined to 0.005 per cent in the neighborhood of its 1.1 per cent natural abundance. Lecompte and coworkers (26) described an infrared analysis for D_2O of greater than 96 per cent purity which is based on the 1.66 μ absorption band, probably $\nu_1+\nu_3$ of HDO. The uncertainty in D content is less than 0.1 per cent.

Liquid scintillation counting techniques for tritium have been described by Farmer & Berstein (27), Hayes & Gould (28), and by Roucayrol (29). Liquid scintillation techniques for C^{14} have been given by Hayes, Hiebert and Schuch (30). Scintillation counting has been used in high pressure diffusion studies for *in situ* analysis of C^{14} by Caskey & Drickamer (31) and of H^3 by Jeffries & Drickamer (32).

Herr (33) described a radiometric analysis for Li^6 in which unknown $LiCO_3$ and standards known from mass spectrometer analysis are placed in contact with a nuclear photographic plate and irradiated with neutrons. The plate blackening by the Li^6 (n,α) H^3 reaction is measured. Samples up to 18 per cent Li^6 were run. The precision of 0.3 per cent Li^6 is about what has been obtained by optical and nuclear resonance methods (34).

Isotope Abundances and Their Variations in Nature

Alpher & Herman (35) reviewed theories of the origin and abundance distribution of the elements. This field is of great interest in its own right as well as because current isotope abundance distributions may be regarded as an original distribution modified by fractionation, radioactive decay, and cosmic radiation. The authors feel that their theory of nuclide formation by neutron capture reactions in the expanding universe has fewer difficulties than other theories.

Ingerson (36) reviewed the subject of nonradiogenic isotopes in geology. Cosmic radiation produces tritons in the atmosphere which combine with oxygen, giving rain water with H^3/H^1 ratios between 5×10^{-18} and 40×10^{-18}. Libby (37) discussed possible tracer applications of natural tritium over a time scale determined by its half-life. He considered applications to the age of rain and agricultural products, the mean storage time of rain or snow before appearance in a water supply, vertical mixing in air masses, and the manner in which an air mass acquires moisture over land.

Fireman (38) remeasured the cross section for $n+N^{14}=C^{12}+H^3$, proposed by Libby as one source of natural tritium, and combined it with cosmic ray neutron data to estimate a triton production rate of 0.1–0.2 $cm.^{-2}$ $sec.^{-1}$, averaged over the earth's surface. Cosmic rays eject tritons at about three times this rate, giving a total of world reservoir of 50 to 110 million curies of H^3. From the He^3 content of the atmosphere Fireman estimates

a mean escape time of 3 to 6 million years for He^3. This is consistent with a temperature of 1500°K at the base of the exosphere.

Paneth and co-workers (39) reported on the He^3 and He^4 contents and their rather small variation with depth in a large iron meteorite. The He^3 amounts to about 30 per cent of the He^4. The He^3 and most of the He^4 come from nuclear reactions induced by cosmic rays. This group (40) has also estimated ages for a large number of meteorites from the uranium and thorium contents and the estimated radiogenic He^4. Maximum ages of a few hundred million years were found. Special experimental techniques for the determination of the very small amounts of He and of uranium and thorium were discussed by Chackett *et al.* (41) and by Dalton *et al.* (42). Martin (43) gave a theoretical discussion of the production of He^3 and He^4 in meteorites by cosmic rays.

Craig (44) made a definitive study of C^{13}/C^{12} ratios in several hundred carbon samples from various geologic sources. Ratios were determined to 1 part in 10^4 and showed a 4.5 per cent range of variation. Equilibrium constants were given as a function of temperature and show that, in general, oxidized and reduced compounds concentrate C^{13} and C^{12} compounds, respectively. Diamond is intermediate in behavior. Speculations on the origin of a graphite sample by isotopic analysis alone are unreliable, due largely to inadequate theoretical treatment of this mineral. Terrestrial organic carbon and carbonate rocks are well defined groups, the latter being richer in C^{13} by about 2 per cent. Marine organic carbon is intermediate. Fossil wood, coal, and limestones show no correlation of C^{13}/C^{12} ratio with age. Petroleum is generally believed to be derived from marine organisms but contains too little C^{13}. This suggests a subsequent isotopic fractionation, such as also seems to have occurred in black shales and carbonaceous schists. However, coal has apparently retained essentially the isotopic composition of its source material. Meteorite analysis indicates that iron carbide concentrates C^{12} more than graphite. The enrichment of the earth's surface in C^{13} may have been due to similar fractionation and a sinking of carbide to the depths.

Wickman (45), continuing studies on C^{13}/C^{12} variations among plants, concluded that metamorphism does not alter the C^{13} abundance of coals. Craig (44) came to the same conclusion. Wickman suggested that carbonates in coals may not always come from plant carbon dioxide.

Anderson (46) wrote an interesting review on certain aspects of natural C^{14}. He discusses the experimental C^{14} activity of contemporary carbon, amounting to 16.6 ± 0.6 dis. gm.$^{-1}$ min.$^{-1}$, the theoretical estimate of 19 ± 4 dis. gm.$^{-1}$ min,$^{-1}$, the fractionation factor of 1.10 ± 0.02 by which C^{14} prefers shell carbonate to wood, and the system employed for low level C^{14} counting.

Results were reported from the Yale (47) and Copenhagen (48, 49) dating laboratories. The Yale laboratory finds a smaller fractionation of C^{14} between contemporary shell and wood than indicated by the concordant

results of the Chicago (50) and Columbia (51) dating laboratories. Buchanan, Nakao & Edwards (52) reported work with living snails and a synthetic C^{14} aquarium which supports the Chicago and Columbia results for fractionation of C^{14} between organic matter and shells. Knowledge of C^{14} fractionation factors is essential for accurate age estimates.

Friedman (23) reported extensive and precise results on the deuterium content of natural waters. Oceanic and U.S. fresh waters ranged from 0.0153 to 0.0156 and from 0.0133 to 0.0154 atom per cent, respectively. Vapor pressure differences in isotopic waters contribute to many results, such as the parallel concentration of deuterium and O^{18}. Light waters evaporating preferentially in equatorial regions leave a heavy residue and precipitate at higher latitudes. Deep ocean water is depleted in deuterium. A similar depletion in O^{18} may be associated with melting ice masses and suggests a penetration of polar bottom currents as far as the equator. Fractional precipitation of Pacific Ocean moisture in passing over mountains was suggested as contributing to the lightness of Great Lakes waters. Similar considerations and evaporation were used to explain river water compositions. A number of suggestive miscellaneous results, e.g., from Yellowstone Park, were given.

Baertschi (53) measured O^{18}/O^{16} ratios for 91 natural waters, including rain, snow, subterranean waters, and water from mineral dehydration. The effects of rain water and evaporation on river water were considered. There is a low O^{18}/O^{16} ratio in terrestrial melt waters. The effect of temperature on rate and equilibrium in exchange between water and rock was examined. Hydration to form gypsum concentrates O^{18} with a 0.35 per cent isotope effect, and the conclusions to be drawn from natural gypsum deposits are discussed.

Several papers appeared bearing on the paleotemperatures of waters. The method is based on the temperature dependence of O^{18} fractionation between these waters and the $CaCO_3$ content of marine skeletons laid down in them. No work has yet appeared on the simultaneous use of a phosphate and carbonate thermometer, proposed to eliminate the assumption of the identity of the present and ancient waters in O^{18} content. Epstein & Mayeda (54) discussed accurate O^{18}/O^{16} ratios for 103 samples of marine and fresh water in an effort to understand their variations. Evaporation contributes. Meltwaters from ice and snow, as in cold ocean currents, decrease salinity and O^{18} content. Epstein & Lowenstam (55) discussed the limitations on the paleotemperature determinations arising from the temperature dependence of the skeleton deposition rate and from sample characteristics which usually preclude study over short growth periods. In general, no single species can give averages and ranges for the water paleotemperatures. These authors investigated the temperature-shell-growth relationship of recent and interglacial Pleistocene shoal-water biota from Bermuda, finding that the present and ancient temperatures are the same to 1–2 degrees. Emiliani & Epstein (56) used the O^{18} content of the $CaCO_3$ of fossil shells to study paleotemperatures in the Lower Pleistocene Lomita marl of southern

California. Temperatures of shallow waters varied from 12° to 30°C. One main colder and one main warmer period may have been due to interaction of marine currents and local changes in the earth's crust. Epstein *et al.* (57) worked out a more reliable process for destroying the organic matter in marine skeletons. This aided them in constructing a revised calcium carbonate-water temperature scale which shows a 0.6° standard deviation in deposition temperature.

Reynolds (58) redetermined the isotopic constitution of Si, Ge, and Hf. Results for Si agree better with the results of Hibbs (59) and of White & Cameron (59), than with the recommendation of Bainbridge & Nier (59). The Ge results differ a little from those of Graham *et al.* (60) perhaps due to mass discrimination in their instrument. The Hf results differed systematically from those of Hibbs (59); it was suggested that high purification might alter the isotopic constitution slightly. The abundance of Hf^{182} is less than 0.003 per cent.

Reynolds & Verhoogen (61) reported on Si^{30}/Si^{28} ratios in 14 minerals and rocks. The probable error of only 0.35 per mil in their ratios is unusually small for a mass spectrometer not employing double collection. In general, the Si^{30} content decreases in going from high to low temperature minerals. The greatest separations occur when deposition is from an aqueous phase rather than a silicate melt. The trends in Si^{30}/Si^{28} usually follow those of the O^{18}/O^{16} ratio for silicates given by Silverman (62). However, the range of variation of Si^{30}/Si^{28} is only about 3 per mil. compared to 33 per mil for O^{18}/O^{16} (62). It was suggested that the silicon had fewer favorable opportunities for exchange processes than carbon or oxygen. Thus, oxygen in silicates may have participated in an isotopic exchange equilibrium with water.

Schwander (63) gave O^{18}/O^{16} ratios for 70 silicate minerals and rocks of magmatic, metamorphic, and sedimentary origin. The samples were quantitatively converted to CO for the mass spectrometer by heating with graphite in vacuum to 2000°C. The first material crystallizing from magma is relatively richer in O^{18}. The highest ratios were in sedimentary rocks, as found also by Silverman (62) and discussed by him. These rocks show a considerable spread in ratios, perhaps due to a variable, incomplete isotopic equilibration with water which depends on surface to volume ratio. Thus, diatomite has a higher ratio than kernels of quartz sand.

Thode, Macnamara & Fleming (64) considered sulphur isotope fractionation in nature. This material was discussed by Thode in last year's review on isotopes.

Fleming & Thode (65) found a threefold variation of A^{36}/A^{38} ratios in 4 pitchblende minerals of different age and uranium concentration. A tendency for low ratios to go with high uranium content may be due to interactions of α-particles and spontaneous fission neutrons with elements near argon. The authors state that mineral age determinations based on K^{40} decay to A^{40} may be in error if the correction for normal A^{40} is based on A^{36}, especially in uranium minerals.

Aldrich *et al.* (66) discussed variations in the abundances of the strontium isotopes. For commercial strontium they are in excellent agreement with Nier. The decay of Rb^{87} to Sr^{87} allows mineral age determinations, if correction can be made for nonradiogenic Sr^{87}. However, these workers have shown that unexplained variations in Sr abundances in minerals at present prevent application of the method to minerals rich in common Sr. Biotite is suitable, and lepidolite has been used. Davis & Aldrich (67) and Tomlinson & Das Gupta (68) described the application of the isotope dilution technique to determination of Rb^{87} and Sr^{87} and the age of lepidolites and biotites.

Friedman & Irsa (69) remeasured Ru isotope abundances using electrical detection and the vapor of ruthenocene, $C_{10}H_{10}Ru$. The atomic weight of 101.08 agrees well with an earlier value of Mattauch; exactly with a value obtained from $RuCl_3 \cdot 5NH_3$ decomposition, but poorly with the accepted atomic weight of 101.7 obtained from oxide decomposition.

Walker & Thode (70) found abundances in natural neodymium to be in satisfactory agreement with previous determinations. They also obtained relative cross sections by observing the depletions due to neutron capture.

Collins, Russell & Farquahar (20) determined the isotopic constitution of Pb ores, which were dated from Pb^{207}/Pb^{206} ratios in associated uranium minerals. From these and earlier data of Nier, the age of the earth's crust was estimated at 3.5 billion years using the Holmes model, which is briefly discussed. An upper limit of 5.5 billion years to the age of the elements arises from the fact that a greater age would imply a negative original Pb^{207} abundance. Ehrenberg (71) reported the ages of several uranium minerals from the Pb^{207}/Pb^{206} ratio, applying corrections for natural Pb.

Kulp, Broecker & Eckelman (72) discussed various methods of age determinations for uranium minerals. They tested a method based on the Pb^{206}/Pb^{210} ratio in which Pb^{206} is found from mass spectrometer analysis and Pb^{210} is found from its α-emitting descendant, Po^{210}, several months after separation of $PbCl_2$ from the mineral. Their values for minerals covering an age range of 60 to 1400 million years agree well with the best ages by other methods. The data suggest the smallness of radon leakage from their minerals. Houtermans *et al.* (73) described similar work, involving counting of RaE (Bi^{210}) β-rays a few weeks after the lead salt separation.

Curran (74) reviewed the determination of geologic age by radioactivity, considering the use of C^{14}, various Pb, Th, and U isotopes, and the use of the ratios Sr^{87}/Rb^{87}, K^{40}/A^{40}, and K^{40}/Ca^{40}.

Isotope Effects and Behavior in Equilibrium Systems

Armstrong, Brickwedde & Scott (75) gave a preliminary report on the vapor pressures of the liquid and solid deuteromethanes. They represented their data by equations of the form $T \log (P_D/P_H) = A - B/T$, where P_H and P_D refer to the vapor pressures of ordinary methane and the particular deuteromethane to which A and B apply. P_H and P_D cross over within the experimental range of 70° to 112°K. Values of P_D/P_H at a given temperature

do not form a geometric progression as the number of substituted hydrogen atoms increases; this assumption has sometimes been made for intermediate substituted water and ammonias. Johns (76) represented his relative vapor pressures for liquid and solid $C^{12}O^{16}$ and $C^{13}O^{16}$ by equations of the form ($T \log (P_{12}/P_{13}) = A - B/T$. The vapor pressure of $C^{12}O$ is roughly 1 per cent higher than that of $C^{13}O$. Davis & Schiessler (77) reported vapor pressure measurements of perdeuterobenzene and perdeuterocyclohexane relative to the hydrogen compounds. The deutero compounds have the higher vapor pressure in the experimental range 10° to 85°C. A plot of log $(P_{C_6D_6}/P_{C_6H_6})$ or of $T \log (P_{C_6D_6}/P_{C_6H_6})$ against T^{-1} is unusual in appearance.

Jones (78) found the triple point temperature of tritium oxide to be 4.49°C. The triple point temperature of D_2O is 3.81°C., for comparison. Lagemann, Gilley & McLeroy (79) measured densities of supercooled D_2O and ultrasonic velocities in stable and supercooled H_2O and D_2O. From these data they calculated adiabatic compressibilities. The compressibility of D_2O is greater, either at the same temperature or in corresponding states based on freezing points. The properties of the stable and supercooled species lie on a single smooth curve.

Perlman, Bigeleisen & Elliott (80) studied the catalyzed gaseous equilibrium $NH_3 + HD = NH_2D + H_2$ in the range 210 to 295°K, representing their constants by $K = 0.972\ e^{509/T}$. The derived zero point energy difference between NH_3 and NH_2D, 635 ± 3 cm.$^{-1}$, is more accurate than can now be estimated from spectroscopy.

In 1947 Bigeleisen & Mayer (81) presented formulas and tables for the free energy difference of isotopic species. In 1953 Bigeleisen (82) gave a similar treatment for the entropy, enthalpy, and heat capactiy. Applications to absolute reaction rate theory were discussed.

Stranks & Harris (83) computed the ratios of the partition functions for the C^{12} and C^{14} isotopic forms of 18 ions and molecules containing one carbon atom. An equilibrium constant of 1.168 at 298.16°K was calculated for $C^{14}O + C^{12}O_2 = C^{12}O + C^{14}O_2$. This is favorable for C^{14} enrichment, and active MnO_2 was suggested as a possible catalyst. Carbon-14 obtainable from the U. S. Atomic Energy Commission currently averages about 12 per cent C^{14}, and work is in progress to raise this figure (10).

The properties of He^3 and He^4 at low temperatures have been studied vigorously in recent years. Pure liquid He^3 has shown none of the unusual properties which are associated with the λ-point in liquid He^4. This result is sometimes taken to indicate that the λ-point is closely connected with the condensation of a Bose-Einstein gas. Reviews on the properties of liquid He^3 and He^3-He^4 solutions have been given by Daunt (84) and by Abraham, Osborne & Weinstock (85).

Nuclear spin alignment and the associated entropy decrease in liquid He^3 have been of considerable interest. Pomeranchuk (86) predicted that antiparallel spin orientation should start below roughly 1°K, so that the

corresponding entropy of R ln2 should decrease about linearly with temperature. There have been speculations based on the accurate vapor pressure data of Abraham, Osborne & Weinstock (87) of the Argonne National Laboratory as to the manner in which this entropy is lost as a function of temperature. However, entropies of liquid He^3 evaluated in this way may not be reliable for temperatures too far below 1.02°K, the lowest temperature of the vapor pressure measurements. Thus, Chen & London (88) claim that these vapor pressures do not require an abrupt removal of entropy, which has sometimes been suggested, and are consistent with an entropy curve going smoothly to zero at 0°K, which is close to a theoretical curve for a Fermi-Dirac smoothed potential liquid below 1°K.

Weinstock, Abraham & Osborne (89) discussed the implications of their melting curve (liquid-solid equilibrium) (90) for the entropy of He^3 (l). Making the reasonable assumption that the nuclei of the solid would be randomly oriented at least down to 0.01°K, this group concluded that there was no appreciable alignment in the liquid above 0.5°K.

Roberts & Sydoriak (91) of the Los Alamos Laboratory have made specific heat measurements on He^3 (l) from 0.54° to 1.7°K. They conclude that the entropy of the liquid is R ln2 at approximately 0.50°K, and that nuclear alignment commences at or above this temperature.

De Vries & Daunt (92) reported specific heat measurements to $\pm$ 10 per cent for He^3 (l) between 1.3° and 2.3°K. These measurements are remarkable in having been made on a sample corresponding to only 8 cc. N.T.P. of gas. Specific heat measurements are also being made by the Argonne group (93).

Fairbank *et al.* (94) concluded from nuclear magnetic susceptibility measurements that nuclear orientation in liquid He^3 was random down to 1.2°K. These direct measurements are being extended to lower temperatures.

The most detailed phase data on He^3-He^4 solutions are due to Daunt & Heer (95) and especially to Sommers (96). In 1953 several theoretical papers dealt with these data, but discussion of them will be left to the reviews on Cryogenics and Solutions of Nonelectrolytes.

Sommers (96) noted that his data implied absorption of heat on isothermal mixing of He^3 (l) and He^4 (l). Sommers, Keller & Dash (97) found this quantity to be 0.17 cal. $mole^{-1}$ at 1.02°K and 8.6 per cent He^3. The free energy of mixing was estimated to exceed the ideal value by 0.23 cal. $mole^{-1}$. The entropy of mixing is then less than the ideal value by 0.06 cal. $deg.^{-1}$ $mole^{-1}$ or 10 per cent. The heat of mixing was thought to be a lower limit, so that the entropy of mixing may be closer to the ideal value.

Isotope Effects in Rate Processes

Isotope effects in chemical kinetics.—Isotope effects in the decarboxylation of normal and substituted malonic acids have continued to be an active subject. The intramolecular isotope effect relative to C^{12} is defined as

$\delta_x = 100(k_4/k_3 - 1)$. The intermolecular effect is $\beta_x = 100(k_1/2k_3 - 1)$.

$$C^xO_2H \xrightarrow{k_3} C^xO_2 + C^{13}H_3C^{12}O_2H$$

$$C^{13}H_2 \begin{cases} C^{13}O_2H \xrightarrow{k_4} C^{13}O_2 + C^{12}H_3C^xO_2H \\ C^{13}O_2H \end{cases}$$

$$C^{12}H_2 \begin{cases} C^{13}O_2H \\ C^{13}O_2H \end{cases} \xrightarrow{k_1} C^{13}O_2 + C^{12}H_3C^{12}O_2H$$

In 1953 Yankwich & Stivers (98) found δ_x for malonic acid at 137°C to be 2.8 ± 0.2 for C^{13} and 10.2 ± 0.9 for C^{14}; the values for bromomalonic acid at 117°C, were 2.4 ± 0.3 and 11.6 ± 0.4. Bigeleisen & Friedman (99) calculated temperature independent values of 2.0 and 3.8. Thus, as with earlier work considered by Bigeleisen and by Thode in the two previous reviews, the theoretical and experimental values are in better agreement for C^{13} than for C^{14}. For malonic acid, C^{12} and C^{13} have so far been determined by mass spectrometry and C^{14} only by its radioactivity. It is desirable to analyze entirely by mass spectrometry, utilizing the high precision of simultaneous collection instruments if possible. In 1952 Stevens, Pepper & Lounsbury (100) used single collection mass spectrometry for C^{12}, C^{13}, and C^{14} in mesitoic acid decarboxylation and found δ_{14}/δ_{13} to be 2.7 ± 0.3, rather than the theoretical value of about 2.

Ratios of C^{14} to C^{13} intramolecular isotope effects in rates of decarboxylation have tended to exceed the theoretical value of about 2 by somewhat more than estimated experimental error. However, Pitzer & Gelles (101) suggested that δ_{13} might be low because of the nuclear magnetic moment of C^{13}. They estimated that the paramagnetic Dy^{+3} ion at a distance of a few angstroms would cause an inhomogeneous magnetic field comparable to that due to a C^{13} nucleus at one end of a C—C bond. They observed that the rate of decarboxylation of phenylmalonic acid in solution at 45°C. was about 10 per cent faster in the presence of 0.5 *N* Dy^{+3} than in the presence of the diamagnetic Y^{+3} ion at 0.5 *N*.

Yankwich, Belford & Fraenkel (102) found the C^{13} intermolecular effect for malonic acid to vary from 4.5 to 3.4 per cent in going from 56° to 129°C. using 80 per cent H_2SO_4 as solvent. The effect is about that given by Bigeleisen's (103) revised calculations. There may be a discrepancy in the temperature dependence if the 56°C. experiments are correct. This could be due to a solvent effect of which the theory naturally takes no cognizance. The reason for using a solvent should be mentioned. The isotopic composition of the first 1 per cent CO_2 evolved is used to obtain β_x. Since appreciable decarboxylation occurs before solid malonic acid is completely melted, there is danger of getting an anomalously low temperature dependence, and the authors suggest that this was the case in the work of Lindsay, Bourns &

Thode (104). Yankwich & Belford (105) determined the intermolecular effect for normal malonic acid in quinoline solution in the range 34° to 118°C. They thought that the significant difference between the isotope effect and its temperature coefficient from their values in 80 per cent H_2SO_4 and in Bigeleisen's model (103) might be due to the complicating entrance of the solvent into an equilibrium which precedes the rate determining step. The theoretical value of β_{13} is not of high accuracy; however, β_{14}/β_{13} should be about 2 (103), neglecting a Pitzer-Gelles effect.

An effective mass m^* for the transition state along the reaction coordinate occurs in absolute rate theory. In considering isotope effects in reactions formulated as bond ruptures, Bigeleisen (103), following Slater (106), took m^* as the reduced mass of the atoms at the ends of the bond. Some reactions may better be formulated as three center reactions in which a bond is formed between A and B and simultaneously broken between B and C. Bigeleisen & Wolfsberg (107) extended Slater's treatment to this situation and obtained an expression for the ratio of isotopic rate constants. For zero and infinite values of a parameter p the expression reduces to the extreme cases of B-C rupture and A-B formation. For $p=1$, B does not move, and its replacement by an isotope gives no rate effect. Comparison with some reactions of isotopic carbon, nitrogen, and oxygen showed that p was close to zero.

Schmitt & Daniels (108) reported on the hydrolysis of urea at 100°C. and pH 5, finding the isotope effects of C^{13} and C^{14} relative to C^{12} to be 5.5 ± 0.3 and 10.1 ± 0.5 per cent. Theoretical estimates agree satisfactorily. A previous study of the enzymatic hydrolysis of urea at pH 5 and 30°C. had given effects of 3.2 ± 0.2 and 10.0 ± 0.1 per cent (109). Simultaneous collection mass spectrometry was used for all three carbon isotopes in both investigations.

Whittle & Steacie (110) gave data in the range 130° to 420°C. for most of the possible reactions of CH_3 and CD_3 radicals with H_2, D_2, and HD. CH_3 and CD_3 react about equally fast with a given isotopic hydrogen molecule. At 210°C. either CH_3 or CD_3 abstracts H from HD 1.7–1.8 times faster than D from HD. Part of this result may be due to the moments of inertia in the activated complex. Thus, $I(CH_3—H—D)/I(CH_3—D—H)$ has a theoretical value of 1.5. The temperature dependence of the isotope effects is uncertain for some of the reactions, and the treatment of this reaction by absolute rate theory is as yet incomplete.

Several studies of C^{14} isotope effects on the rates of organic reactions have appeared from the Oak Ridge group. They are interested in uncovering effects which could lead to errors in interpretation of tracer studies, and many of the reactions are not amenable to theoretical treatment. Bonner & Collins (111) found a 4 per cent effect in the reaction of ozone with stilbene-α-C^{14} to form the molozonide. Bonner & Collins (112) also showed that an isotope effect occurs in the permanganate oxidation of a secondary carbinol to the ketone but not in oxidation of the ketone to the acid. They also reported C^{14} effects in catalytic hydrogenation ranging from 2 to 11.5 per

cent (113). Ropp, Raaen & Weinberger (114) found effects to occur in the decomposition of mercurous formate and in some C^{14}-keto group reactions, but no effects were found in bromine addition to a labeled double bond, in a Diels-Alder reaction, and when pure CO_2 was bubbled through either of two alkaline media. The last conclusion is of interest in connection with similar studies by Baertschi and Craig considered below.

Baertschi (115) found that bean seedlings utilize $C^{12}O_2$ faster than $C^{13}O_2$ by a factor of 1.026 ± 0.001. Urey (116) found a factor of 1.029 in the assimilation of dissolved CO_2 by one-celled algae. Baertschi found no isotope effect during the respiration of germinating beans. The origin of the isotope effect is obscure, but it is not the same, as once suggested, as that which occurs when carbon dioxide is absorbed by hydroxide. Thus, Craig (44) found a fractionation factor of 1.014 on bubbling a CO_2-air mixture through barium hydroxide. Baertschi (117) found C^{13} fractionation factors of 1.014 ± 0.002 and 1.011 ± 0.001 on bubbling a CO_2-N_2 mixture through barium hydroxide and on exposing pure CO_2 to a film of sodium hydroxide solution, respectively. His second result agrees with kinetic theory collision rates. The factor 1.014 of Craig and Baertschi seems to indicate fractionation in the absorption process, since a rate determining diffusion through excess air or nitrogen should give a fractionation factor of 1.004 (44). Baertschi (117) also found that the fractionation factor between $C^{12}O_2^{16}$ and $C^{12}O^{16}O^{18}$ was only 1.001. This observation may be related to the work of Becker & Beyrich (118), who found that $C^{12}O^{16}O^{17}$ and $C^{13}O_2^{16}$ behave differently in a thermal diffusion column, although they have almost identical masses. The asymmetric molecule may make more efficient collisions since its rotational quantum number need change only by one, compared to the change of two required for the symmetric molecule.

Buchanan, Nakao & Edwards (119) found that, in the uptake of CO_2 by algae, the C^{14} isotope effect relative to C^{12} is 2.39 ± 0.04 times greater than that for C^{13}. This seems more reasonable than the much larger ratio implied by the data of Weigl & Calvin (120).

Isotope effects in transport processes.—Becker, Misenta & Stehl (121) measured the viscosities of *ortho*- and normal-deuterium gas by a precise differential method. In the region 16.6° to 20.3°K, *o*-D_2 has a viscosity higher than that of *n*-D_2 (2/3 *ortho*) by 0.06 per cent. Previous work by Becker & Stehl (122) showed that *p*-H_2 had a higher viscosity than *n*-H_2 (1/4 *para*). Becker *et al.* (121) note that it is the nonrotating species, *o*-D_2 and *p*-H_2, which show the larger viscosities. For H_2 Halpern & Gwathmey (123) had predicted larger differences and of opposite sign than observed. Halpern (124) later predicted that gaseous He^3 should show a greater viscosity than He^4, even after correction for the mass effect. Detailed calculations below 5°K were subsequently presented by de Boer & Cohen (125), who noted a marked influence of nuclear spin and statistics as well as of the choice of intermolecular potential field. According to these calculations the viscosity

of He^3 can be about twice as large as calculated from the viscosity of He^4 with a simple mass correction. In 1953 a preliminary report was given of work by Becker and co-workers (126) on the viscosities of pure gaseous He^3 and He^4 between 1.3° and 4.2°K. Agreement with the calculations of de Boer and Cohen was indicated, confirming also the qualitative prediction of Halpern.

Rowlinson (127) measured the ratio of the viscosities of H_2O and D_2O vapors to about 1 per cent, finding η_{D_2O}/η_{H_2O} to be about 1.5 per cent higher than the value 1.054 computed from the masses. For the liquids, the ratio varies from 1.305 at 278°K to 1.146 at 398°K. Pople (128) commented on the viscosity of isotopic substances, pointing out two circumstances, in either of which the square root of the mass law may be applied: (*a*) all masses are changed in the same ratio, e.g., H_2 and D_2, but not H_2O and D_2O; (*b*) the intermolecular forces are functions only of the distance between the centers of mass, e.g., approximately spherical species such as CH_4 and CD_4, but not liquid H_2O and D_2O. Pople's conclusions were based on classical mechanics.

Wang, Robinson & Edelman (129) measured tracer diffusion coefficients of HDO, HTO, and H_2O^{18} in ordinary water up to 55°C. At 25°, the values of $D \cdot 10^5$ cm.^{2} sec.$^{-1}$ are 2.34 ± 0.08 (HDO), 2.44 ± 0.06 (HTO), and 2.66 ± 0.12(H_2O^{18}). The difference between HTO and H_2O^{18} was attributed to the larger moments of inertia and lower energy of HTO in its intermolecular torsional oscillations. Sitting lower in a potential well, the HTO would then have a higher activation energy for diffusion. The authors plan to refine their technique for the measurement of these small effects. The present results support previous work by Wang (130) in indicating that special mechanisms involving fast hydrogen ion transfer, such as are thought to be important in electrolytic conduction, are negligible in self-diffusion, and that the process is carried out by single H_2O molecules in thermal equilibrium with the semi-crystalline water lattice.

Meyer & Eigen (131) found that, due to compensating isotope effects, the thermal conductivity of liquid D_2O was only about 3 per cent less than that of H_2O in the range 10° to 60°C.

Caskey & Drickamer (31) reported thermal diffusion ratios, α, for $C^{14}O_2$–$C^{12}O_2$ up to 160 atm. and from $-15°$ to 50°C. Strong variations of α with density were observed. Near the critical temperature α changed sign as many as three times and showed a deep negative minimum value. Some results are in qualitative agreement with the theory of irreversible processes. There is complete disagreement with the Chapman-Enskog theory, perhaps because of the role of orientation with CO_2. Jeffries & Drickamer (32) studied diffusion in the system CH_4-CTH_3 up to 300 atm. and from 0° to 50°C. Agreement with the Enskog dense gas theory, except at the highest pressures, is probably due to the approximately spherical symmetry of the molecules and the distance from the critical temperature region. Cuddeback, Koeller & Drickamer (132) measured tracer diffusion coefficients from 0° to 50°C.

and up to 10,000 atm. in THO-H_2O and in S^{35}-tagged sulfuric acid and sulfate solutions. Curves of the diffusion coefficients as a function of pressure show maxima and minima. An interpretation of the behavior was attempted in terms of an activation volume and the tetrahedrally coordinated structure of water. It seems, for example, that the initial increase of diffusion coefficient with pressure may be due to a breakdown in the water structure.

Klemm and co-workers (133) reported on the silver isotope effect in electrolytic migration in molten silver chloride. They gave a theoretical discussion of this and previous data.

Jones (134) measured the relative diffusion constants of He^3 and He^4 through vitreous silica in the range 0° to 500°C., finding $D_3/D_4 = (1.16_6 \pm 0.01_5)\ e^{-(61\pm7)/RT}$ (slight revision of published value). The slightly higher activation energy for He^3 may be due to its higher vibrational energy in the activated state where the He is close to lattice atoms. The experimental activation energies of the isotopes differ by about 1 per cent.

Among the most important studies involving differences in isotopic behavior are those concerned with the transport properties of liquid He isotopes. Guttman & Arnold (135) reported on a search for participation of He^6 in the superflow of liquid He^4 below its λ-point. The He^6 (0.82 sec. half-life) was present at an atom fraction of 10^{-19}. The concentration of He^6 in material emerging from the superleak was at most a few per cent (actually 4 ± 7 per cent) of the concentration at the entrance of the leak. The authors point out that this result is consistent with the Bose-Einstein gas model for liquid He^4. However, attention was also drawn to a prediction of Landau & Pomeranchuk, not involving B—E statistics, that no dilute impurity, including He^6, would participate in the He^4 superflow.

Hammel & Schuch (136) have reported that the He^3 as well as the He^4 component of liquid He^3—He^4 solutions passes through superleaks at a rate independent of pressure gradient. For the data so far reported the He^3 rate is only a few per cent of that of the He^4 component, but it is much greater than that of pure He^3(l) at the same temperature and pressure. The flow properties of pure He^3(l) are classical. It may not be justifiable at present to designate this behavior of He^3 in He^3—He^4 solutions as a participation in superflow. Such participation has not so far been understandable theoretically, although it is not necessarily excluded in a theory of liquid helium recently proposed by Temperley (137).

The velocity of second sound in liquid He^4 and in He^3—He^4 solutions has been activity studied. This is the velocity, u_2, with which heat waves are propagated in such media below the λ-point. The temperature dependence of u_2 for dilute solutions of He^3 in He^4 has been controversial. Pomeranchuk predicted a maximum in u_2 at about 1°K, and a decrease to a small finite value at 0°K, while Dingle predicted that u_2 would approach $u_1/\sqrt{3}$ as for pure He^4 (u_1 is ordinary sound velocity). In 1953 King & Fairbank (138) reported data down to 0.25°K for 0.3 and 4.3 per cent He^3 solutions which agree with Pomeranchuk's predictions.

Use of Isotopes in the Study of Mechanisms

In this application isotope effects are usually ignored, although this must be done with caution in the case of the hydrogen isotopes. The N^{15} work is discussed in one group, since the nitrogen to nitrogen bond is always of central importance. Gas reactions, reactions involving solids, and solution processes are then considered.

Friedman & Bigeleisen (139) studied the thermal decomposition of N_2O to N_2 and O_2 at 750°C., using $N^{15}N^{14}O$ and $N^{14}N^{15}O$. They showed that no atom equilibration occurred in N_2, and that NO neither exchanged with N_2O nor catalyzed equilibration of N_2. These results make unlikely a chain mechanism proposed by Pease, and support a unimolecular decomposition.

Amell & Daniels (140) studied the exchange rate of the gas reaction $N^{15}O_2 + N_2O_5 = NO_2 + N^{15}NO_5$, obtaining rate constants agreeing within experimental error with those for the reaction between N_2O_5 and NO. This result supports the view that $N_2O_5 \rightarrow NO_2 + NO_3$ is the initial step in N_2O_5 decomposition and in the N_2O_5—NO reaction.

Holt & Hughes (141) found that azobenzene formed from hydrazobenzene in ethyl alcohol at 150°C. must come from a hydrazobenzene molecule without rupture of the N—N bond: $2\phi HN-NH\phi \rightarrow \phi N=N\phi + 2\phi NH_2$. Thus, azobenzene cannot arise from recombination of ϕN radicals. A mechanism involving a cyclic dimer of hydrazobenzene is consistent with these results but disagrees with older work indicating first-order kinetics for a substantial fraction of the reaction.

Clusius & Vecchi (142) found the thermal decomposition of N^{15}-labeled N,N-diphenylhydrazine at 270°C. to be represented by $3\phi_2N^{14}N^{15}H_2 \rightarrow 3\phi_2N^{14}H + N^{15}N^{15} + N^{15}H_3$. They explained this result by a mechanism involving the radicals ϕ_2N^{14}, H_2N^{15}, and $\phi_2N^{14}N^{15}H$.

Higginson & Sutton (143) determined the isotopic composition of N_2 produced in the oxidation of N_2H_4 by various oxidizing agents. They used an excess of ordinary N_2H_4 along with some containing 33 per cent N^{15}. It was suggested by Higginson, Sutton & Wright (144) that oxidation by 1-electron-transfer oxidizing agents and by complex oxidizing agents involves the simultaneous occurrence of the two limiting reactions: (*a*) $N_2H_4 \xrightarrow{-(e)} \frac{1}{2}N_2 + NH_3$, and (*b*) $N_2H_4 \xrightarrow{-4(e)} N_2$. Higginson and Sutton then conclude that in (*a*) the nitrogen atoms in half the nitrogen molecules come from the same hydrazine molecule, while in the other nitrogen molecules the atoms come from different hydrazine molecules. In (*b*), which is also the sole reaction for 2-electron-transfer oxidation and for all alkaline oxidations, there is no fission of the N—N bonds. Mechanisms consistent with these results were given in the above two papers.

Clusius & Vecchi (145) dissolved $N(CH_3)_4N^{15}O_3$ in carefully dried liquid N_2O_4 and showed that quantitative nitrogen exchange occurred between the solvent and nitrate radical. They suggested the presence of small amounts of NO^+ and NO_3^- in the solvent as an explanation.

Clusius & Hürzeler (146) studied the oxidation and reduction of hydrazoic acid in which one terminal azide nitrogen was N^{15}-labeled. The isotopic compositions of the N_2, formed in all cases, and of the other products were consistent with bond breaking at a terminal nitrogen of the azide group, except for the isotopic composition of some N_2O formed in the reaction with permanganate.

Coillet & Harris (147) studied the exchange of atomic deuterium with CH_4 at 350°C. They considered two reasonable possibilities: (*a*) the H abstraction $D+CH_4 \rightarrow CH_3+HD$, followed by rapid exchange of CH_3 radicals with D atoms before stabilization as a deuteromethane; and (*b*) the inversion process $D+CH_4=CH_3D+H$. Process (*a*) should lead to CD_4 as a major exchange product, while (*b*) should give CH_3D. Over 80 per cent of the product was CD_4, and thus (*a*) seems to be the main process.

McNesby, Davis & Gordon (148) investigated the pyrolysis of a mixture of ordinary and deuteroacetone at 500°C. The analysis of the methane produced supports a Rice-Herzfeld free radical mechanism and excludes any appreciable amount of intramolecular reaction.

Maybury & Koski (149) studied the D_2—B_2H_6 exchange between 25° and 75°C., finding the reaction to be three-halves order with respect to diborane. In going from high to low pressures the order with respect to D_2 shifted from zero to one. These facts are consistent with dissociation into a borine radical, its exchange with deuterium adsorbed on the wall to give a partially deuterated borine radical, and a rate determining reaction of the deuterated borine with diborane. A recombination of borine and deuterated borine radicals, which occurs predominantly at the walls, seems required to explain the smallness of the effect of surface to volume ratio. The exchange reaction between normal and completely deuterated diborane seemed to be predominantly homogeneous and showed a total order of three-halves. The results were explained by a rate determining collision between diborane and borine.

Ogg & Sutphen (150) observed a rapid catalysis of the equilibrium $O^{16}O^{16}+O^{18}O^{18}=2O^{16}O^{18}$ by isotopically normal ozone at room temperature. The thousandfold slower rate of O^{18} exchange with ozone showed that the above equilibrium was not established through reaction 1. A mechanism involving steps 2, 3, and 4 was proposed, involving atomic oxygen obtained from a small amount of ozone decomposition. Only about one-thousandth

$OOO + OO^{18} \rightarrow OOO^{18} + OO$	k_1	1
$O_3 \rightarrow O + O_2$	k_2	2.
$O + O_2 \rightarrow O_3$	k_3	3.
$O + OO^{18} \rightarrow OO + O^{18}$	k_4	4

of the intermediates in 3 and 4 are effectively stabilized to give ozone exchange by 3, but this number is increased by foreign gases. Johnston & O'Shea (151) showed that the above oxygen equilibrium was established in

the presence of mercury vapor by irradiation with λ2537. They confirmed Ogg and Sutphen by concluding that equilibration went through a chain reaction involving step 4, which is initiated by oxygen atoms produced by mercury sensitization.

Gutmann (152) has studied the ammonia-deuterium exchange on nickel and iron powders in the range 210° to 319°C. A small deviation from the first order exchange law may be due to isotope effects. The exchange rate on iron was independent of ammonia pressure, first order with respect to deuterium, and showed an activation energy of 17.5 kcal./mole. There is a discrepancy among various workers with regard to the orders. The catalytic behavior of Ni was not reproducible.

Cameron, Farkas, & Litz (153) have studied O^{18} exchange in the systems V_2O_5—O_2, V_2O_5—H_2O, V_2O_5—H_2O—O_2 from the range 400° to 550°C. The V_2O_5—O_2 exchange showed the first order kinetics expected of a surface reaction. A zero order oxygen dependence suggests that this reaction proceeds through strongly adsorbed surface oxygen. No definite assignment can be made of the 45 kcal. $mole^{-1}$ activation energy to the surface processes. The exchange rate in the V_2O_5—H_2O reaction was 20 to 30 times faster than V_2O_5—O_2. The similarity of H_2O—O_2 exchange rates in the presence of V_2O_5 to those with V_2O_5—O_2 suggests that the latter process controls the rate. The above work involved a surface-controlled reaction on alundum-supported V_2O_5. Heat treatment caused the unsupported V_2O_5—O_2 exchange to change from a surface to a diffusion-controlled reaction, presumably due to recrystallization and the annealing of defects.

Kemball (154) studied CH_4—D_2 exchange on evaporated films of rhodium, platinum, palladium, and tungsten. As in a previous study with nickel, two different mechanisms seem to be operative: one produces CH_3D and the other gives CH_2D_2, CHD_3, and CD_4. Markham, Wall & Laidler (155) extended Kemball's theoretical treatment of his data with nickel. Adsorbed CH_3D is considered to be formed from adsorbed CH_3 radicals and D atoms, and adsorbed CH_2D_2, CHD_3, and CD_4 are considered to be formed from adsorbed CH_2 radicals and D atoms. These are fast surface reactions. Desorption of the products is in each case the slow process. With a reasonable choice of parameters, the calculated rates of production of all four methanes agree with experiment.

The use of deuterium is contributing to our understanding of the mechanism of catalytic hydrogenation. In 1953 Bond & Turkevich (156) reported on the reaction of propylene with deuterium over a platinum catalyst in the range −18° to 130°C. The present experiments, as well as others cited, show that during the interaction of deuterium with double bonds, hydrogen and deuterium atoms redistribute themselves among the product molecules. Thus Bond and Turkevich found propanes containing 0 to 8 deuterium atoms. The kinetics suggest that the surface reaction involves chemisorbed propylene molecules and deuterium atoms, and that both addition and redistribution occur through the reaction of half-hydrogenated states with

deuterium atoms. Detailed understanding of the distribution of product species is not possible at present.

Bigeleisen, Bothner-By & Friedman (157) found negligible C^{13} fractionation in the pyrolysis of barium adipate at 350°C. to give barium carbonate and cyclopentanone. In the pyrolysis of a mixture of barium adipate and radioactive barium carbonate, all C^{14} remains in the latter. As a mechanism they suggest a rapid, reversible proton removal from an α-carbon atom in the adipate ion, followed by a rate determining step in which carbonate is eliminated and the ring closed. An argument was given to show that the isotope effect expected from this mechanism should be less than 1 per cent at 350°C., in agreement with experiment.

Haul, Stein & de Villiers (158) studied the exchange of $C^{13}O_2$ with calcite from 300° to 800°C. at a CO_2 pressure maintained well above the dissociation pressure. They explain their data by a rapid initial exchange at surfaces and boundaries which is accompanied by a slower diffusion-controlled exchange. In the latter process, it was suggested that carbonate momentarily breaks up into an oxide ion and a CO_2 molecule. The latter passes to a similar neighboring site to reform a carbonate ion.

In 1952 Stranks and Harris found no carbon isotope effect in reaction 1

$$Co(NH_3)_4CO_3^+ + H_2O + 2H^+ = Co(NH_3)_4(H_2O)_2^{+++} + CO_2 \qquad 1.$$

while Hunt, Rutenberg, and Taube showed from O^{18} tracer studies on the related reaction 2 that the C—O, not the Co—O, bond is broken in carbonate release

$$Co(NH_3)_5CO_3^+ + 2H^+ = Co(NH_3)_5H_2O^{+++} + CO_2. \qquad 2.$$

The apparent inconsistency of these observations led Posey & Taube (159) to study 1 using H_2O^{18}. They found that the CO_2 was unenriched, and that only one-half of the oxygen in the product complex came from the solvent. They point out that their results and those of Stranks and Harris are consistent with the mechanism

$$Co(NH_3)_4CO_3^+ + H^+ + H_2O \rightarrow Co(NH_3)_4H_2OCO_3H^{++} \quad \text{slow} \qquad 3.$$

$$Co(NH_3)_4H_2OCO_3H^{++} \rightarrow Co(NH_3)_4(H_2O)^{++} + CO_2 \quad \text{complete.} \qquad 4.$$

No large carbon isotope fractionation is expected in 3, the proposed rate determining step in which the Co—O bond is broken, and none is expected in 4, in which the C—O bond is broken but which goes to completion.

Bunton & Llewellyn (160) used O^{18} as a tracer to show that in the hydrolysis

$$[RCO_2 \cdot Co(NH_3)_5]^{++} + OH^- = [Co(NH_3)_5OH]^{++} + RCO_2^-$$

there appears to be a gradual shift from Co—O to C—O fission in going from the weakly acidic acetic acid ligand to the strongly acidic trifluoroacetic acid ligand in the series $R = CH_3$, CH_2Cl, CCl_3, CF_3. On the other hand, there is no evidence for C—O fission for the corresponding reaction of either acetato- or trifluoroacetato-pentamminocobalt(III) ions. These

workers also confirmed the conclusion of Hunt, Rutenberg, and Taube that there is no Co—O fission in reaction 2 of the preceding paragraph.

Wilmarth, Dayton, & Flournoy (161) measured the parahydrogen conversion rate in aqueous alkali, finding it to be homogeneous and first order with respect to H_2 and OH^- concentrations. Exchange of D_2 to give HD as an initial product occurred at a slightly lower rate. A proposed mechanism is (1) $D_2+OH^-\rightarrow D^-+DOH$, followed by (2) $HOH+D^-\rightarrow OH^-+HD$, in which 1 is the slow step. The hydride ion may be solvated. An isotope effect is indicated by the value of 1.61 found at 100°C. for k_{D_2}/k_{HD} in (1); this value does not take account of the fact that only half of the HD reactions produce observable change. Wilmarth & Dayton (162) showed that very rapid parahydrogen conversion and an approximately equal rate of deuterium gas exchange occur in solutions of potassium amide in liquid ammonia. The ammonia and aqueous reactions are analogous, but the rate constant for amide catalysis at −50°C. is 10^4 times as large as that for hydroxide catalysis at 100°C. This striking difference was related to the base strength of the ions.

Weller & Mills (163) used deuterium in a study of the mechanism of homogeneous hydrogenation catalysis by cuprous acetate in quinoline.

Shiner (164) considered the hydrolysis mechanism of tertiary amyl chlorides in connection with isotope rate effects observed with deuterated species.

Gold & Long (165) found that the rate of introduction of deuterium into anthracene in deuterosulfuric acid was 8 to 16 times more rapid at the meso than at the next most reactive position. The rate of removal of deuterium from anthracene in the two-phase system, carbon tetrachloride-sulfuric acid, was 10 to 20 times faster at the meso than at the next most reactive position. The data were discussed in terms of the conjugate acid of anthracene formed by proton addition to anthracene at the meso position.

Isotope Effects and Uses in Structure and Atomic Spectra

Structure.—Pepinsky (166) considered some uses of isotopes in the determination of structure by neutron diffraction. The lower incoherent scattering of neutrons by deuterium has made it useful in the location of hydrogen positions, especially in powder diffraction.

Peterson & Levy (167) reported a single crystal neutron diffraction study of heavy ice which agrees with the original powder diffraction data of Wollan, Davidson, and Shull and the pattern calculated for the Pauling model of ice, in which hydrogen atoms occupy unsymmetrical positions between two oxygens in a disordered structure. The Pauling model also accounts for the residual entropy of R ln(3/2) observed in solid H_2O and D_2O. However, Peterson and Levy state that their results are not definitely incompatible with Bjerrum's (168) considerations on structure and disorder in ice, and Rundle (169) claims that the residual entropy can also be explained by disorder in a Bjerrum type of polar ice structure.[2]

[2] Lipscomb has recently pointed out an error in Rundle's calculation [*J. Chem. Phys.*, **22**, 344 (1954)]. Rundle now concludes that the residual entropy is not yet understood if ice is polar [*J. Chem. Phys.*, **22**, 344 (1954)].

Levy & Peterson (170) investigated four phases of ND_4Br by powder neutron diffraction. This study supports work of other types in showing that the phase III to phase II transformation is one of order-to-disorder and does not involve the onset of free rotation of ammonium ions. The same conclusions apply to ammonium chloride.

In 1951 Nordman & Lipscomb (171) suggested that the anomalous lengthening of short (strong) O—H—O hydrogen bonds on deuterium substitution could be understood in terms of a "box"-like form of potential function. At a given, sufficiently high temperature, the relatively greater population of higher vibrational states in the well for the deuterium compound leads to a greater broadening of the deuterium probability distribution, and thus of the well. In 1953 Rundle (172) pointed out that at low temperatures, where only the lowest vibrational states are occupied, the substitution of D for H should shorten, or at least not lengthen, these strong hydrogen bonds. Lattice constant data for light and heavy ice at 0° and −66° give some support to this view, but Rundle suggested that a larger effect should be found with shorter hydrogen bonds.

Contraction occurs on D substitution in a crystal such as LiH. Nordman & Lipscomb (173) gave a quantitative discussion for LiH, LiD, and LiT, predicting the lattice parameter and expansion coefficient for LiT, which have not as yet been reported.

Lord & Merrifield (174) reported an infrared study of the effect of deuterium substitution in crystals having hydrogen bonds of various lengths. The frequency shifts showed strong dependence on bond distance.

Andrew & Eades (175) measured proton magnetic resonance absorption in polycrystalline C_6H_6 (benzene), C_6H_5D, and 1,3,5-$C_6H_3D_3$. The last compound made possible a separation of the intermolecular and intramolecular contributions to the line width without knowledge of the crystal structure. A narrowing of the absorption on warming from 90° to 120°K was attributed to a reorientation of the molecules about their hexad axes in the lattice with an activation energy of 3.7 kcal. $mole^{-1}$.

Stephenson, Corbella & Russell (176) investigated transition temperatures of the dihydrogen and dideutero phosphates and arsenates of K^+, Rb^+, Cs^+, NH_4^+, and ND_4^+ and of their solid solutions. The entropy changes for the pure compounds were compatible with the Slater model of these transitions. According to this model the hydrogen atoms are randomly located so as to give a disorder entropy of $\frac{1}{2}$ R ln2 just above the transition region, while at higher temperatures this entropy approaches R ln(3/2). Below the transition the hydrogens are ordered. Occupation of deeper lying vibrational levels in the hydrogen bond potential wells may explain the increase in the transition temperature on deuterium substitution: the transitions of KH_2PO_4 and KD_2PO_4 are at 122° and 213°K, respectively. Neutron diffraction studies of KH_2PO_4 by Peterson, Levy & Simonsen (177) and by Bacon & Pease (178) have not been able to establish definitely the double

minimum character of the potential function associated with the hydrogen bonds.

Atomic spectra.—Isotope shifts in the wave lengths of atomic lines are due to changes in mass and in nuclear structure. For light atoms the mass shift dominates. It may be regarded as made up of an elementary mass shift, due to the finite mass of the electron as expressed in the Rydberg formula, and of a specific mass effect arising from the effect on the optical electron of the remaining electrons. The mass shift decreases in going to the heavy elements; it becomes dominated by an isotope shift arising from the change in the interaction of the nucleus with a penetrating optical electron which is caused by the addition of a neutron. On adding a neutron there are, in general, changes in nuclear volume and shape, charge distribution, electric quadrupole moment, magnetic moment distribution, etc. Separated isotopes have been especially helpful among the heavy elements. Reviews of this subject have been given by Foster (179) and by Dieke (180).

Parker & Holmes (181) obtained the shifts of O^{18} relative to O^{16} for 20 atomic lines. After correcting for the elementary mass effect they evaluated two terms occurring in the theory of the specific mass effect from two measured shifts. In general, the calculated shifts of the remaining lines agreed well with experiment.

A number of isotope shifts have been determined among the heavy elements. Krebs & Nelkowski (182) reported shifts for the six ytterbium isotopes, relative to mass 172, at λ5556. The lines of the even isotopes are spaced about equidistantly. The odd isotopes also show approximately this spacing from each other, but they are shifted as a group toward lines of the lighter isotopes. Shifts for masses 171 and 173 are only in rough agreement with rather old calculations. Stukenbroeker & McNally (183) measured Th^{230}—Th^{232} shifts in ThI and ThII spectra. The Th^{232} line always lies to longer wavelength, indicating more tightly bound levels in Th^{230}. Conway & Fred (184) reported shifts for plutonium isotopes 238, 239, and 242, relative to 240. The isotope shift in Bi^{209}—Bi^{210} was reported by Fred, Tomkins & Barnes (185). They also concluded that the nuclear spin of Bi^{210} is zero.

Wilets, Hill & Ford (186) gave a detailed theoretical treatment of atomic isotope shifts and nuclear structure. The constant density spherical nuclear model predicts too large shifts and fails to account for the oscillation of the shift magnitude with neutron number and for the staggering of shifts between even and odd isotopes. It was concluded that the observed shift patterns are consistent with current ideas of the nucleus, when account is taken of compressibility, polarizability, and the regular progression of nuclear shapes. For a test of their formulation, the authors calculated isotope shifts beyond Pb relative to those expected for spherical nuclei of constant density. Direct comparison with observations has not been made, however.

The hyperfine structure of the atomic $^3S_1$ metastable state of He^3 has been studied by Weinreich, Grosof & Hughes (187) by an atomic beam magnetic

resonance method. The accuracy of the splitting is 3000 times that of a previous optical determination and is sufficient to reveal effects due to the structure of the He^3 nucleus (188).

The reviews on Spectroscopy and Microwaves may be consulted for the large number of papers involving isotopes in molecular spectra.

Atomic Masses

Precise atomic masses are of interest in indicating nuclear stability, in checking nuclear disintegration data, and in testing nuclear models.

Ewald (189) reported on the $C^{12}H$—C^{13} doublet, and his C^{13} mass agrees well with that of Li *et al.* (190). Smith & Damm (191) employed the mass synchrometer for the measurement of doublets at masses 28 and 30. This instrument measures the masses of ions in terms of high harmonics of their cyclotron frequencies, and its apparently very precise data are of especial interest for comparison with masses from conventional mass spectrographs. Ogata & Matsuda (192, 193) gave mass differences for 36 doublets through A^{40}, including $C^{12}H_4$—O^{16}. Engler & Hintenberger (194) reported mass differences for doublets at masses 14, 16, 28, and 40, including $C^{12}H_4$—O^{16}. Bainbridge (195) has adopted the mass table of Li *et al.* (190) from n^1 to F^{20}, which is based on nuclear reaction Q-values. In this mass region there is satisfactory agreement between the nuclear reaction and mass spectrographic values. The most serious discrepancy has been for the $C^{12}H_4$—O^{16} doublet and the C^{12} mass, which has been important as a secondary standard in deriving masses of isotopes which cannot be directly compared with O^{16}. Bigeleisen (196) summarized the situation at the end of 1951, when it appeared that the mass spectrographic work of Nier's group (197), Ogata & Matsuda (198), and Mattauch & Bieri (199) gave a higher C^{12} mass than that of Ewald (200) and Bönisch (201), which, however, agreed with that of Li *et al.* (190). Although Ogata & Matsuda (192) reported a measurement in 1953 favoring the higher mass, other considerations favor the lower value. Engler & Hintenberger's value (194) and the mass synchrometer data (191, 194) support the lower mass. Measurements bearing on the C^{12} mass were discussed in several papers of the *Proceedings of the National Bureau of Standards Symposium on Mass Spectroscopy in Physics Research (1951)* (202). It appears there that Mattauch and Bieri have withdrawn their value.

Duckworth and co-workers (203) gave mass differences for the pairs Zr^{92}—Mo^{92}, Zr^{94}—Mo^{94}, Zr^{96}—Mo^{96}, and Ru^{96}—Mo^{96} and compared them with nuclear disintegration data. Hogg & Duckworth (204) made a number of mass measurements and studied mass trends for $28 \leq N \leq 50$ and $28 \leq Z \leq 40$. They found previously indicated enhanced nuclear stability at neutron numbers 28 and 50 and proton number 28. There was no indication of subshell structure. These authors (205) also determined 40 masses for $82 \leq N \leq 126$. This region is of generally enhanced stability, but no subshell structure was indicated within experimental error. These workers reveal enhanced stability due to shell structure by plotting the difference between observed

and smooth semiempirical masses, such as those of Metropolis & Reitwiesner (206), against neutron or proton numbers. Ewald (207) gave a graphical representation of the energy-valley surface on the basis of recent mass measurements, which indicated irregularities at neutron magic numbers 2, 8, 20, 28, 50, 82, and 126. The evidence for proton magic numbers from this source was slight. An account of the evidence for shell structure from the energetics and cross sections of nuclear reactions is given by Blatt & Weisskopf (208).

The book, *Experimental Nuclear Physics, Vol. I*, edited by Segrè (195), contains a detailed treatment by Bainbridge of the charged particle dynamics encountered in various types of mass spectrographs. He discusses atomic masses derived from such instruments and from nuclear reaction data, as well as isotope abundances. A book by Ewald & Hintenberger (209) appeared which covers the general field of mass spectroscopy, including applications to other fields. The *Proceedings of the National Bureau of Standards Symposium on Mass Spectroscopy in Physics Research (1951)* (202), published in 1953, contains about 35 papers dealing with a variety of topics. Hollander, Perlman & Seaborg (210) gave a summary in tabular form of data on radioactive and stable isotopes.

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RADIOACTIVITY AND NUCLEAR STRUCTURE[1]

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In preparing this review we have followed the plan of restricting attention to a few topics which either have been particularly active in the past year or have not been reviewed in this series in the past few years. It was also thought desirable to provide some background information in each section in order to make the discussion as intelligible as possible to those who do not follow nuclear work closely. In so doing it was necessary to sacrifice a complete treatment of new information.

Nuclear Structure and Nuclear Shells

The electronic shell structure of atoms has been explained successfully by the methods of quantum mechanics on the basis of three basic hypotheses: first, that the force which is responsible for electronic binding is largely a pure coulombic attraction, dependent only upon the distance r between the electrons and the nucleus; second, that the electron has an unchanging, intrinsic angular momentum, or "spin"; and third, that the Pauli exclusion principle is operative, placing an upper limit on the number of electrons which can occupy a given atomic shell.

The energy levels of the simplest atomic system, the hydrogen atom, can be calculated exactly from the quantum mechanical equations. More complicated atoms must be treated by mathematical approximations; for not only does the simple coulomb force between electron and nucleus cease to be exactly correct because of shielding effects of the electrons on each other, but also the complexity of the equations soon precludes their exact solution. In spite of these difficulties, it is still possible to understand the electron shell structure of atoms, and to correlate the observed chemical properties with those which would be expected from their structure.

The situation with the atomic nucleus is still more complicated, for besides the same mathematical difficulties in solving many body wave equations, the basic law of force between nucleons in the nucleus is not known. Thus, one does not even know what equation it is which one cannot solve. The problem then is to account for the properties of nuclear states without a detailed knowledge of nuclear forces and without the hope that a rigorous formulation can be attained. These properties include the binding energies of nuclei, their mechanical and magnetic moments and their electric quadrupole moments, all of which are measurable entities. One would like to find that these properties could be correlated with some systematic order of

[1] The survey of the literature pertaining to this review was concluded in January, 1954.

quantum states corresponding to the addition of successive protons and neutrons just as atomic properties are correlated with electron configuration. With respect to some properties, singular success has been realized with the "independent particle model or shell model" of nuclear structure (1, 2). Other properties were best explained in terms of "collective" features as, for example, when the nucleus is treated as a liquid drop in describing nuclear fission (3, 4). Largely within the past year a synthesis of these two obviously dissimilar types of nuclear motion has been developed by Hill & Wheeler (5) and by Bohr (6). In this new model, formulated in quantitative terms by Bohr & Mottelson (7), a coupling is introduced between the motion of independent particles and collective motions of the nucleus. Some applications of this theory will be reviewed here and compared with treatment of the same problems by refinements of the independent particle model.

Aside from the properties of stationary nuclear states such as those mentioned, a theory of nuclear structure should be extendible to explain transitions between nuclear states. As examples, the configurations assigned to a pair of isobars (nuclei of equal mass number) must be compatible with a theory for β-decay between these isobars, and types of configurations assigned to different energy levels must conform with the observed γ-ray transitions between these levels with respect to lifetimes, internal conversion coefficients, and angular correlations.

As experimental data have been improved in recent years it is becoming apparent that any of the models so far suggested falls short of giving a complete detailed picture. A primary difficulty is that mathematical formulation is possible only with simplifying assumptions which usually impose some extreme set of conditions. Those nuclear properties which are not affected by the imposed conditions will appear to be explained while others will not. Similarly, it might be expected that a particular model will describe a particular property in limited regions among the nuclei because the approximations are, in effect, fulfilled for these cases.

Although "nuclear spectroscopy" hardly presents a unified picture at present, the development within the past few years has, for the first time, provided grounds for correlating many nuclear properties and, in some instances, is attaining a remarkable certainty of prediction.

Independent particle model.—The special significance of even numbers of neutrons and protons relevant to nuclear structure has long been recognized (8). If we consider a nucleus with an even number of neutrons, for example, the binding energy of an additional neutron is considerably lower than that of a second neutron which again results in an even number. One of the manifestations of this form of stability is the predominance among the naturally occurring elements of those isotopes with even numbers of both neutrons and protons (even-even type).

As far as is known experimentally, all even-even nuclei in their ground states have zero spin [total angular momentum (9)], and implied even parity. It is inferred from this that irrespective of their quantum states,

even numbers of like particles couple to spin zero (in contrast to Hund's rule). In the independent particle model, the nuclear spin (and parity) of an odd mass nucleus is assumed to be that of the odd nucleon, which is characterized by independent motion in an averaged field determined by the even-even remainder. In simplest form, the only intimate relation of the even-even remainder to the odd nucleon is through the Pauli exclusion principle which prevents the odd nucleon from assuming a quantum state already occupied.

A test of this proposition lies in seeing whether one can calculate a logical sequence of quantum states which agrees with the observations. An important series of check points are the so-called magic numbers, such as 50, 82 and 126 which are nucleon numbers of special stability analogous to the closed shells in electron structure (10). The assumptions made in establishing an order of quantum states should also provide some mechanism for completing shells at these points.

The system which best delineates the positions of the magic numbers and has had a great deal of success in predicting parities and spins is that given independently by Mayer (1) and by Haxel, Jensen & Suess (2). The potential acting upon the particle is taken to be that of an approximately rectangular well, that is, one which has a constant negative value within nuclear dimensions and rises sharply to zero at the edge of the nucleus. The order of levels so obtained is modified in one important respect: it is arbitrarily assumed that there is a strong spin orbit coupling which splits the levels into pairs corresponding to angular momenta $j=l+\frac{1}{2}$ and $j=l-\frac{1}{2}$ with the $l+\frac{1}{2}$ levels lying lower. Furthermore, it is assumed that the splitting becomes greater as the orbital angular momentum (l) takes on larger values. It is at these points that the major shell closures are attained. The order in familiar spectroscopic notation is, according to Mayer:

$$\begin{array}{l|l|l|

spins which cannot be attributed to single unpaired particles (9, 11, 12). The spin of Se^{79}, for example, has been found (12) to be 7/2, whereas the shell model would predict that this nuclide, with 45 neutrons, should have available only spins of 9/2, 5/2, 3/2, or 1/2. In quite a few cases there is also evidence from radioactive decay data for a low-lying 7/2 state in the $g_{9/2}$ shell (13).

The single particle shell model has also been applied to predict other ground state properties of nuclei such as magnetic moments and electric quadrupole moments, but here with only qualitative success. The quadrupole moments are found experimentally to be larger in magnitude than can be accounted for by the shell model; i.e., by a single proton or neutron within a spherical well (5, 7, 14 to 16). The magnetic moments deviate considerably from the extreme regularity which this model would predict (17, 18, 19).

The application of the independent particle model to a variety of phenomena was reviewed by Flowers (20) and the reader is referred to this article for a discussion which shows the surprising success of the model. That the extreme independent particle model cannot account for properties in detail is not unexpected, and by its nature it is not concerned with high-lying excited states of nuclei nor with the states of even-even nuclei. A few examples of extensions of the model will be covered in succeeding sections.

Two seemingly different approaches are being employed to explain phenomena which either are not covered by independent particle considerations or for which this extreme model is inadequate. In one system, Edmunds & Flowers (21, 22) have extended the single particle model by examining not only the odd particle but also the configurational interactions of all particles outside closed shells. Similarly, deShalit & Goldhaber (23) have shown that through such interactions, one group of nucleons may influence another, shifting energy levels and, in general, resulting in mixed configurations. Near a closed shell where the core is stable the wave functions of the independent particle states may be relatively "pure" for the ground states and low-lying excited states. In regions well removed from closed shells the mixture of configurations is extreme.

The other approach (5, 7, 24) considers the interaction between independent particle wave functions and those for collective modes of motion of the nucleus. In the Bohr and Mottelson formulation two basic types of readily excitable modes of motion are considered:

(*a*) That of individual nucleons (or holes) outside of closed shell configurations; (*b*) Surface wave motion of lowest order, assumed to be the collective nuclear motions of low energy.

The two classes of motion are not independent of one another but are coupled. Consideration of this coupling leads [as shown earlier by Rainwater (14)] to the conclusion that nuclei not possessing doubly closed shell configurations generally prefer spheroidal rather than spherical shapes. This conclusion is borne out by the experimental values of the quadrupole moments, which are too large to be explained by the single particle model but

which, nevertheless, do correlate with shell structure. The coupling of the surface and single particle motions may be considered strong in regions well removed from closed shells and this leads to interesting consequences which will be examined presently.

Excited states of even-even nuclei.—Because there is no example to the contrary, it is assumed that the ground states of all even-even nuclei have zero spin and even parity, designated 0+. A wide range of experimental data show that the first excited states of such nuclei are 2+ (25 to 29). This conclusion comes principally from measurements of the internal conversion coefficients of gamma rays. Experiments also indicate that the second excited states are either 2+ or 4+. It is not possible to choose between the different nuclear models on the basis of spins and parities of the first excited states of even-even nuclei since most models predict spin 2, even parity.

The energy spacings between these states are also of interest. The energy of the first excited state has been observed to decrease in general with increasing mass number but rises at each closed shell number. For a nucleus with closed shells for both neutrons and protons the spacing between the ground state and first excited state is abnormally large (25 to 29).

In the mixed configuration approach of deShalit & Goldhaber (23), the smooth variation of energy level of the first excited state is explained by the multiplicity of neutron and proton configurations capable of having spin 2. These interact in such a way as to decrease the energy of the mixed state. As a closed shell for one type of particle is approached the number of such states decreases and at the closed shell the particle type involved cannot participate at all and a maximum energy for the 2+ state results. Unfortunately, it is not yet possible to apply this treatment quantitatively to see if the actual energy level spacings can be accounted for.

The states of even-even nuclei have been attacked in detail in terms of collective aspects of nuclear motion. Ford (24) has calculated energy level spacings and has found the trends to be in qualitative agreement with observations including the breaks at the closed shell numbers. Modifications to the "strong-coupling approximation" are required to give reasonable quantitative values for the energies in the calculable cases near closed shells; this is as expected, since this approximation should break down near closed shells.

One of the interesting consequences of the strong coupling approximation of Bohr & Mottelson (7) is that it gives rise to a nuclear level pattern similar to the energy state pattern of polyatomic molecules. The nuclear matter in the tidal bulges contributes to an effective rotational moment of inertia. Thus, the theory predicts bands of quasi-rotational levels in nuclei, the levels being more closely spaced the larger the spheroidal distortion. For even-even nuclei with zero spin ground states only the rotational levels of even J are expected to appear due to symmetry considerations. The theory predicts rotational energies approximately proportional to $J(J+1)$ as in molecules.

The theory also predicts vibrational excited states of higher energies in analogy to molecular spectra.

Rotational states of even-even nuclei in regions away from closed shells have recently been identified experimentally, by their very striking properties: regularities of spins and parities, characteristic energy trends, and very large transition rates between levels (30). From a study of the α-particle spectra of the heavy elements (well beyond lead), Asaro & Perlman (27) have noted the systematic occurrence of a rotational spectrum including the fundamental mode (ground state) and at least two excited states. The quantitative agreement with energy level spacing predicted by Bohr and Mottelson for regions well removed from the closed shells is excellent. As one approaches the double closed shell nucleus $_{82}Pb^{208}$, the energy spacings begin to deviate from the pure rotational spectrum, again in agreement with theory.

Experimental verification for the predicted "vibrational" excited states in nuclei is lacking.

γ-ray transition lifetimes and coulomb excitation of nuclei.—One of the pieces of evidence for single particle behavior in odd mass nuclei was the agreement found between experimentally observed γ-ray lifetimes (intensities) and those calculated by Weisskopf (31) from a simple one-particle model. But Goldhaber & Sunyar (32) had pointed out in 1951 that certain γ-ray transitions between low-lying excited states of even-even nuclei exhibit lifetimes much too short (transition probabilities too great) to be accounted for by single particle behavior; these must indicate the collective nature of the nuclear excitation. It is interesting to observe that in these cases the ratio of observed transition probabilities (33 to 36) to those expected from single-particle behavior increases as one moves away from closed shells, a behavior which parallels the degree of expected particle-surface coupling (7).

The short lifetime of γ-ray transitions such as these is related to the nuclear charge deformation or intrinsic quadrupole moment; indeed, from the observed transition times the electric quadrupole moments may be calculated (7). A reflection of the same interaction is the induced excitation of the nucleus by an external coulomb field. The coulomb interaction can be distinguished experimentally from other modes of nuclear excitation by irradiating nuclei with protons or α-particles of energy insufficient to bring them within the range of the nuclear forces. Such coulomb excitations which have been discussed for some time are now well established experimentally (37 to 40). Here the cross section for the excitation gives a measure of the quadrupole moment and reflects the collective nature of the transition (7). The excited states which are observed are those which have been attributed to rotational states from other evidence cited above.

Anomalous nuclear spins.—Both the extended independent particle model of Edmunds & Flowers (21, 22) and the collective model of Bohr & Mottelson (7) can explain the appearance of low-lying levels with spin $j-1$ in shells of given j, thus accounting for the cases of 7/2 ground state spins and low-lying 7/2 excited states observed to occur in the $g_{9/2}$ shell.

β-decay and the shell model.—The success of the single particle shell model in predicting the spins and parities of nuclear energy states has not been limited to correlations of radiative (γ) transitions between these states. The β-decay process, in which a nucleus $(Z)^A$ is transformed into $(Z+1)^A$ or $(Z-1)^A$ by the emission of a negative or positive electron (respectively), has provided another testing ground for this model, inasmuch as the selection rules for β-decay involve primarily the changes of spin and parity.

The criterion most widely used in the empirical classification of β-decay data as "allowed" or "forbidden" to various degrees has been the *ft* product or comparative half-life, in the Fermi theory of β-decay (41, 42, 43). The *f* is a theoretical factor which corrects the observed half-life *t* for the effects of the nuclear charge and the energy of the transition, thus reducing all half-lives to a comparable basis. It has been found from analyses of the large body of β-decay data (44, 45) that the *ft* values fall into several groups, not perfectly resolved, but indicative of the ranges of "allowed" and "forbidden" transitions.

The spins and parities available from the shell model have, with few exceptions, given agreement with the categorization offered by these empirical *ft* groupings. Ordinary allowed transitions, which obey the selection rule $\Delta J=0, \pm 1$, no parity change, exhibit *ft* values averaging around 10^5 sec. Other groupings of larger *ft* values can also be correlated with states available from the shell model.

Consider, as an example, the radioactive sulfur isotope, S^{35}, which decays to Cl^{35} with a half-life of 87 days and an energy release of 167 kev. These properties give S^{35} an *ft* product of 1×10^5 seconds, placing it in the empirical "allowed" group. From the single particle shell model, one predicts that in both S^{35} and Cl^{35}, the odd particles should occupy a $d_{3/2}$ ground state. The β-transition between these two states, then, should obey the selection rule $\Delta J=0$, no parity change, which is consistent with the observed *ft* product of S^{35}. (The spins of both S^{35} ane Cl^{35} have been verified experimentally as 3/2, lending further support to the shell states.)

In spite of wide qualitative success, however, one of the principal inadequacies in the extreme single particle model has manifested itself in the course of examination of these *ft* products. One troublesome instance has been the observation that there are two definite and resolved groups of *ft* values corresponding to "allowed" transitions in that the $\Delta J=0, \pm 1$ (no parity change) selection rule is obeyed. The normal (sometimes called *unfavored*) allowed transitions have *ft* values centering around 10^5 sec., while another small group (called "superallowed") exhibit roughly fiftyfold greater transition probabilities; i.e., *ft* values $\sim10^3-10^4$ sec. This striking difference is not accounted for by the shell model, which would consider only the initial and final spin and parity quantum numbers.

The nuclei which undergo "superallowed" β-decay are the so-called mirror pairs; these are isobars each of which has an equal number of protons and neutrons plus an extra particle (proton or neutron), as for example $_8O^{15}$ and $_7N^{15}$. As a rule, the higher *Z* isobar decays by positron emission to the

lower, the extra proton changing to a neutron. From the standpoint ofnuclear forces, the mirror pairs are practically identical, so their β-decays should be relatively uninfluenced by detailed differences in nuclear structure of parent and daughter, differences which apparently cannot be neglected in other cases.

The decay probabilities of the simplest mirror nuclei have thus become a kind of norm for quantitative comparison of allowed and forbidden transition rates with predictions from the shell model. Thus, an "unfavored factor" has been defined as the ratio of the observed lifetime to that calculated from the shell model for transitions between pure single particle states (as can occur in mirror nuclei). These retardation factors seem to average $\sim$50 for both the normal allowed and forbidden transitions.

An explanation for the general retardation of the β-decay process has been given by the collective nuclear model of Bohr & Mottelson (7), which points out that nuclear states in general differ not only in the quantum numbers of individual particles but also in their collective properties, particularly the shape of the nuclear surface; this equilibrium nuclear shape may be distorted appreciably from sphericity, in regions not near closed shells. If a change in the nuclear shape accompanies the β-transition, the transition probability will be reduced. Such retardations are quite analogous to the operation of the Franck-Condon principle in molecular spectroscopy, where electronic transition probabilities also involve a vibrational overlap integral. The mirror pairs of nuclei are expected, because of their symmetry, to possess almost identical surface shapes, with no attendant retardations in β-decay; this would account for their "superallowed" nature.

The study of *ft* values has further revealed several cases, in regions near closed shells, where the expectations from the shell model have been violated quite badly. One example will be cited: The β-decay of $_{36}Kr^{85}$ to an excited state of $_{37}Rb^{85}$ takes place with an *ft* product of $\sim 10^9$ sec., although independently it has been shown that both initial and final states are $g_{9/2}$ so the selection rule for an "allowed" transition is obeyed. Thus, one might have expected an *ft* value nearer to 10^5 sec. (46). DeShalit & Goldhaber (23) have attempted to explain the occurrence of such "super-slow" β-transitions by a somewhat different extension of the single particle model. If the proton and neutron configurations in nuclei are not pure "single particle" states, but instead involve mixtures of available states, then the transition rates may be altered. In the case of Kr^{85}, the simple transfer of a particle from a $g_{9/2}$ neutron state to a $g_{9/2}$ proton state (which would certainly exhibit an "allowed" *ft* value) might be illustrated as follows:

	$_{36}Kr^{85}$		$_{37}Rb^{85}$
neutron shell	(38 core) + $(p_{1/2})^2$ + $(g_{9/2})^8$ + $(g_{9/2})^1$	$\beta^- \rightarrow$	(38 core) + $(p_{1/2})^2$ + $(g_{9/2})^8$
proton shell	(36 core)		(36 core) + $(g_{9/2})^1$

But the process actually taking place is apparently not this simple. De-

Shalit and Goldhaber have shown that, for example, the presence of a $g_{9/2}$ proton may have a stabilizing effect on pairs of $g_{9/2}$ neutrons, so that the final neutron state in Rb^{85} may be a mixture of

$$\boxed{(38\text{ core}) + (p_{1/2})^2 + (g_{9/2})^8} \quad \text{and} \quad \boxed{(38\text{ core}) + (g_{9/2})^{10}}$$

with the latter configuration predominating. The β-decay from Kr^{85} would then involve not only the transfer of an unpaired neutron to a proton but a rearrangement of the neutron core structure as well. This latter effect would be responsible for a noticeable retardation in the transition rate.

It will be interesting to note how the Bohr-Mottelson theory on the one hand and the preceding explanation of deShalit and Goldhaber on the other may complement each other in the further development of a consistent picture of nuclear structure. The Bohr-Mottelson collective model has its greatest applicability in the middle of shells where the existence of large mixtures of configurations may have an averaging effect equivalent to the assumption of a deformable core, while the picture of relatively pure configurations discussed by deShalit and Goldhaber may be fruitful near closed shells. As in many previous theoretical advances, the relative usefulness of the various models may depend both on the particular situation to which they are applied and also on the ability to overcome the mathematical complexities involved in their application.

Reactions of Nuclear Transmutation

The years 1947–1951 witnessed the development of many new particle accelerators in the 100 Mev range and their use in the study of high energy "spallation" reactions, reactions in which scores of fragments are emitted from the highly excited target nuclei. It became commonplace for chemists to isolate, in the complex mixtures of reaction products, elements whose atomic numbers were as much as 20 or 30 below that of the target element. The particles accelerated in these "high energy" devices were, as in previous cyclotrons, hydrogen, deuterium, and helium ions. Templeton & Seaborg (47) have, in a previous review, summarized from a radiochemical view the salient features of these reactions.

Since that time, the field of high energy nuclear transmutations has been enhanced by several new avenues of research. Among these have been: radiochemical studies of nuclear reactions induced by mesons, studies of reactions induced by protons accelerated to several billion volts, and thirdly, studies of reactions caused by cyclotron accelerated "heavy" ions, i.e., ions such as carbon, nitrogen, and oxygen. Turkevich (48) has reviewed thoroughly the radiochemical studies of meson-induced reactions; we shall confine this survey to the last two subjects.

Reactions with billion volt protons.—The Brookhaven proton synchrotron, or "Cosmotron," accelerates protons to a maximum energy of 2.2 Bev, the highest energy yet achieved in a man-made device.

Hudis *et al.* (49) have studied the reactions of 2.2 Bev. protons with aluminum ($_{13}Al^{27}$), and have compared the yields of the products Na^{24}, Na^{22}, F^{18}, N^{13}, C^{11}, and Be^{7} with those observed earlier by Marquez & Perlman (50), using 335 Mev. protons. It is found that with the exception of light fragments such as Be^{7} the yields do not change markedly between these two energies, indicating that in the average encounter the amount of excitation energy transferred to the target nucleus by the incoming proton is relatively independent of bombardment energy, over this range. The yield of Be^{7} is reported to be sixfold higher at 2.2 Bev than at the lower energy; whether there are additional energy requirements for the production of these light fragments, or whether some other mechanism becomes operative, has not been stated.

Reaction yields have also been determined (51) for about forty radioactive nuclides produced by the interaction of 2.2 Bev protons with copper ($_{29}Cu^{63,65}$). A novel feature of the results is that the yields of all products observed seem to be fairly constant over the whole range of product elements isolated. This is in contrast to the rapid drop-off in yields with decreasing mass number (of the product nucleus) which is observed at 340 Mev. (52).

One of the interesting aspects of the new "billion-volt-chemistry" is the prominence of secondary reactions, i.e., reactions which could not have been caused by the beam of high energy protons, but must have been initiated by nuclei which were themselves primary reaction products. Isotopes of gallium, germanium, and arsenic (atomic numbers two, three, and four higher than that of copper) have been chemically isolated from copper targets by Sugarman and Turkevich (53), who report small but measurable yields. Batzel, Miller & Seaborg (52) had earlier identified gallium and germanium in a similar experiment at 340 Mev, with yields only ~25 per cent and ~10 per cent, respectively, of those now reported at 2 Bev. These results are consistent with the direct observation of greatly enhanced yields at 2 Bev of fragments such as Be^{7}, for it is these light nuclei which initiate the second-order reactions.

Heavy ion acceleration.—Before 1940, no atom heavier than He^{4} had been accelerated in a cyclotron. During that year, Alvarez (54) reported briefly the results of an experiment in which a small beam of stripped C^{12} atoms had been observed in the (original) Berkeley 37-in. cyclotron. Somewhat later, Condit (55) and Tobias and Segrè (56) showed that carbon ions could be accelerated in the Berkeley 60-in. cyclotron; beam intensities were far too low to render nuclear transmutation studies feasible, but some observations were made on the scattering of these ions in cloud chambers and photographic emulsions.

After the war, an effort was made to increase the carbon ion beam current in the 60-in. cyclotron, and in 1950, Miller *et al.* (57) reported that they definitely had observed the following nuclear reactions:

$$_{13}Al^{27} + {}_{6}C^{12} \rightarrow {}_{17}Cl^{34} + {}_{2}He^{4} + n,$$
$$_{79}Au^{197} + {}_{6}C^{12} \rightarrow {}_{85}At^{206} + 4n.$$

The availability of high energy carbon ion beams was of much interest as a research tool in nuclear chemistry, for it makes possible the production in a single bombardment of elements up to six higher in atomic number than the target element. Thus, Ghiorso *et al.* (58) synthesized two isotopes of californium (element 98) from normal uranium by the reactions:

$$_{92}U^{238} + {}_{6}C^{12} \rightarrow {}_{98}Cf^{246} + 4n$$
$$_{92}U^{238} + {}_{6}C^{12} \rightarrow {}_{98}Cf^{248} + 6n.$$

These high energy carbon ions (~100 Mev) have also been used in transmutation studies of lighter elements where they can supplement the utility of other high energy devices, for the e/m of a carbon nucleus is such that only the highly neutron-deficient isotopes of the product $Z+6$ element are produced. The production from copper of neutron-deficient Br^{74} and Br^{75} without the concomitant appearance of heavier bromine isotopes has been demonstrated (59).

Recently, Walker & Fremlin (60), using the University of Birmingham 60-in. Nuffield cyclotron, have accelerated in addition to C^{12} (+6) and C^{13} (+6) ions, $_{10}Ne^{20}$ (+9), $_{4}Be^{9}$ (+4), $_{7}N^{14}$ (+6), $_{6}C^{12}$ (+5), $_{7}N^{15}$ (+6), $_{6}C^{13}$ (+5), and $_{8}O^{16}$ (+6) ions. With their nitrogen ion beam of 125 Mev maximum energy, this group (61) has observed the production of K^{38}, Cl^{34}, P^{32}, Si^{31}, and Na^{24} from aluminum targets. Wyly & Zucker (62), working at the Oak Ridge National Laboratory, have constructed a 63-in. cyclotron for the acceleration of N^{14} (+3) ions to 25 Mev, and have observed a number of reactions with light element targets.

Nitrogen ion beams with energies exceeding 100 Mev have recently been obtained by the Berkeley group (63) at the Crocker cyclotron, and have been utilized by Ghiorso *et al.* (64) to produce isotopes of elements 97, 98, and 99 from normal uranium, in reactions such as:

$$_{92}U^{238} + {}_{7}N^{14} \rightarrow 99^{247} + 5n.$$

Characteristic of most heavy ion beams to date has been their low intensity and extreme energy inhomogeneity, a situation rendering experimentation more difficult but at the same time offering some insight into the mechanism of their acceleration in the cyclotron. The condition for resonance of any ion in a fixed frequency cyclotron is that it have approximately the same charge to mass ratio as the ion for which the machine was designed; this is usually $e/m = \frac{1}{2}$ as in the deuteron or α-particle. (Small differences in e/m can be compensated by a change in magnetic field.) This would correspond in the case of C^{12} to the completely stripped (+6) ion, which would revolve at the same velocity (three times the energy) as a helium ion accelerated in the same machine.

Observations both at Birmingham (61) and at Berkeley (63) have tended to strengthen the idea that the carbon atom is not readily stripped in the central ion source itself, but that the high energy carbon beams owe their existence to the phenomenon of harmonic preacceleration. Doubly charged ions are apparently created at the ion source, and are accelerated at one-third

the velocity (one-ninth the energy) of the fully stripped atom. A small fraction of these +2 ions are stripped further by collision processes and some, which reach +6, get in resonance again and are accelerated to the full radius of the machine. This process leads to the final C^{12} (+6) ions having a continuous distribution in energy extending up to the maximum possible energy for those which happened to have their origin at the center of the cyclotron. By such a mechanism one is able to explain the observation of a very intense carbon beam of low energy in addition to the much smaller C^{12} (+6) beam with its spread of energies.

Because of the energy inhomogeneity of the heavy ion beams, estimates of the cross sections (reaction probabilities) for heavy ion reactions have been, of necessity, very approximate. But they do indicate at least that these ions behave "normally" as nuclear projectiles with cross sections similar to those found with the lighter charged particles. It should be pointed out, however, that in the transuranium element region a very large fraction of the total reaction cross section goes into fission; a fact which adds greatly to the difficulty of synthesizing higher and higher elements (64).

Transuranium Elements

The methods of building higher elements than those which exist in nature consist either of adding the charge directly to the nucleus by bombarding with charged particles or by adding sufficient numbers of neutrons to produce β^--unstable nuclides which decay to higher elements. In general, different isotopes of a particular element are formed by the two methods particularly as elements well beyond uranium are reached. For example, if Cm^{242} is bombarded with deuterons the isotope of element 97, Bk^{243}, is made by the *d*, *n* reaction. If, on the other hand, successive neutrons are added to Cm^{242}, the first berkelium isotope seen would be Bk^{247} (or Bk^{249}), since it can be predicted that Cm^{247} (or possibly Cm^{249}) is the first β^--unstable isotope. Pertinent to these considerations are the energy relations (measured, calculated, and estimated) for all nuclides in the heavy element region; these have been summarized by Seaborg (65). This summary shows which species will be expected to be β-stable as well as the energies for α-emission, and for β^--emission and electron capture for those nuclides which are unstable according to these modes.

Heavy β-stable isotopes.—According to the trends in α-decay properties, the greater the mass number of the isotope of a particular element the lower will be the α-energy and consequently the longer will be the α-half-life (66). The heaviest β-stable isotope is therefore likely to be the longest-lived. (This is not necessarily the case where a series of isotopes bridge a major closed shell, as, for example, is the case for polonium isotopes.)

An important consequence of this situation is the fact that moderately long-lived isotopes of certain unstable elements may yet be prepared. Plutonium may be used as an example. The isotope which has been prepared in large quantities is Pu^{239} with a half-life of 2.4×10^4 years. It is possible by sufficient neutron irradiation to produce the heavier isotope Pu^{242} which

has a half-life of 5×10^5 years (67). It is probable that Pu^{244} is β-stable, and its α-decay half-life can be estimated to be $\sim10^7$ years. Aside from intrinsic interest, these heavy isotopes are also the best starting materials for investigating higher elements. If methods can be refined for producing such long-lived isotopes free of shorter-lived ones, chemical investigations of plutonium would be simpler because of the lesser health hazard.

For elements above plutonium a similar situation applies. The best known β-stable isotope of americium is $\sim$500 year Am^{241}, but Am^{243} is apparently also β-stable and its half-life is $\sim10^4$ years (68). Similarly, the first isotope of curium produced was Cm^{242} which has a half-life of 162 days. This isotope has been produced in weighable quantities but the difficulties of making chemical and physical measurements are very severe with a substance so intensely radioactive. There are now known longer-lived curium isotopes and it can be predicted that some with still greater lifetimes will be prepared. Of the known curium isotopes, Cm^{243} has a half-life of $\sim$100 years (69) and Cm^{244}, 19 years (70). Another isotope, Cm^{245}, has been prepared and a lower limit of 500 years can be placed on its half-life (71). Still others, Cm^{246} and Cm^{248}, will surely be β-stable and have long half-lives (65). That for Cm^{248} will be somewhat greater than 10^4 years. An isotope of californium of interest is Cf^{248} which has a half-life of 225 days (72) and is therefore susceptible to extended chemical experimentation not possible with the short-lived isotopes previously known.

Elements 99 and 100.—Isotopes of element 99 have been prepared in two different ways. Ghiorso *et al.* (64) irradiated uranium (U^{238}) with high energy nitrogen (N^{14}) ions and produced two isotopes of element 99; one of these, which was tentatively assigned to 99^{247} and has a 7.3 minute half-life, was identified by means of its α-particles, while the existence of another assigned to 99^{246} was inferred from the observed growth of Cf^{246}. These isotopes would have arisen from the following reaction type:

$$U^{238} + N^{14} \rightarrow 99^{247} + 5n.$$

Also identified in this irradiation were isotopes of californium and berkelium. Isotopes of element 99 produced in this way will be neutron deficient and decay by electron capture as well as by α-emission, since it can be deduced (65) that the first and probably only β-stable isotope of element 99 is 99^{253}.

Element 99 has also been identified following intensive neutron irradiation of plutonium (73). The reactions here consist of multiple neutron captures interspersed with β^--decay processes. A possible pathway can be shown diagramatically:

$$Pu^{239} \text{ (multiple } n, \gamma) \; Pu^{243} \xrightarrow{\beta^-} Am^{243}$$

$$Am^{243} \; (n, \gamma) \; Am^{244} \xrightarrow{\beta^-} Cm^{244}$$

$$Cm^{244} \text{ (multiple } n, \gamma) \; Cm^{249} \xrightarrow{\beta^-} Bk^{249}$$

$$Bk^{249} \; (n, \gamma) \; Bk^{250} \xrightarrow{\beta^-} Cf^{250}$$

$$Cf^{250} \text{ (multiple } n, \gamma) \; Cf^{253} \xrightarrow{\beta^-} 99^{253}.$$

The half-life for 99^{253} is estimated to be ~1 month.

Further irradiation of the californium fraction by Harvey *et al.* (74) has resulted in the preparation of an α-emitting isotope of element 100, probably 100^{254}:

$$Cf^{253}(n, \gamma)Cf^{254} \xrightarrow{\beta^-} 99^{253}(n, \gamma)99^{254} \xrightarrow{\beta^-} 100^{254}.$$

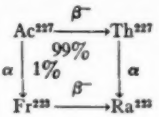
In the cases of the new elements 99 and 100, the isotopic assignments were made from the following considerations. The regularities of chemical properties are such (75) that the elements are presumed to be present as tripositive ions of the actinide series and may be considered as eka-holmium and eka-erbium in correspondence with the rare earth series. They were found to follow the predicted elution sequence in the ion exchange adsorption-elution method for separating actinide elements (75), that is, they were separated from each other and from some lower actinides such as californium and berkelium in the proper order. The mass number assignments were made largely on the basis of the methods of formation and by the agreement with predicted decay properties. In some instances mass number assignments made in this way are unique; in others, they may be off by as much as two units.

The Natural Radioactivities

It is interesting to note that important findings are still being made in the field of natural radioactivity and that, in addition, many studies are being made on the details of decay processes, the aggregate of which is adding substantially to our knowledge of decay processes in general and to the spectroscopic states of the heavy elements in particular. Well over 100 papers on the decay properties of natural substances have appeared in the last year alone. In large part they contain information too detailed for this review so attention is focused on a relatively few reports which deal with new species.

Occurrence of astatine in the actinium family.—For many years it had been thought that element 85 was missed completely in the decay of the natural radioactive families. Then in the period 1943–44, Karlik & Bernert (76) reported that the three "A-products" [RaA (Po^{218}), AcA (Po^{215}), ThA (Po^{216})] have rare β^--branching resulting in astatine isotopes which were too short-lived to be isolated but were detected in the mixture by their α-particles. The difficulty of the experiment is such that accurate measurement of the properties is not possible and in one case, that of At^{216}, it is doubtful that it could have been present because other information indicates strongly that Po^{216} is β-stable.

Recently Hyde & Ghiorso (77) have shown that in the actinium family decay sequence,



the 23 minute Fr^{223} which arises in 1 per cent α-branching of Ac^{227} itself decays to the extent of 4×10^{-3} per cent by α-emission to a new isotope, At^{219}. This isotope of astatine with a 0.9 min. half-life could be isolated chemically, thus proving its atomic number. In turn, At^{219} decays largely by α-emission to Bi^{215}, an 8-min. β-emitter which joins the main series by decaying to Po^{215} (AcA). The two new species At^{219} and Bi^{215} are properly members of the actino-uranium family.

α-radioactivity among the rare earth elements.—The existence of α radioactivity in natural samarium has been known for some time (78) and more recently it has been shown (79) that there are many α-emitters in the rare earth region. These α-emitters have been produced artificially and could not exist in nature because of their short α-decay periods and also because they lie outside of the band of β-stability and are electron capture unstable. The added energy for α-decay possessed by these nuclides as compared with their neighbors is explained by their decay into the region of 82 neutrons with exact analogy to the situation in the heavy element region where the maximum α-decay energy for each element comes in that isotope which decays to a nuclide of 126 neutrons. The slope of the energy surface is such that the maximum α-decay energy is smaller for succeeding lower atomic numbers.

At element 62, samarium, the maximum α-energy should lie in Sm^{146} (84 neutrons) which is absent in natural samarium but is surely β-stable. Its absence can therefore only be explained by an α-half-life of $\sim10^8$ years or less which would have permitted its decay since the elements were formed. The fact that it was not found in many cyclotron irradiations would indicate that its half-life is long, that is, near the upper limit of $\sim10^8$ years. Dunlavey & Seaborg (80) have been successful in identifying Sm^{146} by the nuclear emulsion technique following an intense irradiation of neodymium with 40-Mev α-particles. They attributed the observed 2.55-Mev α-tracks to this isotope and from yield considerations the half-life was calculated to be $\sim5\times10^7$ years.

The next lowest element susceptible to the test of these regularities is neodymium for which the maximum α-energy should appear in Nd^{144} and for which it might be predicted that the energy would be $\sim$0.5 Mev lower than for Sm^{146}. This energy would correspond to an extremely long half-life, and indeed Nd^{144} is a component of natural neodymium for which no α-activity had been detected. Recently Waldron, Schultz & Kohman (81) have impregnated photographic plates with carefully purified neodymium and ob-

served the tracks of 1.9-Mev α-particles. Attributing these to Nd^{144} they were able to calculate a half-life of 1.5×10^{15} years.

On the natural α-activity of bismuth.—Using the nuclear emulsion technique for measuring α-tracks, Faraggi & Berthelot (82) reported that Bi^{209} decays by the emission of a 3.15-Mev α-particle with $\sim 10^{17}$ year half-life. This work was apparently confirmed by Riezler & Porschen (83) who obtained a similar half-life (based on 7 α-tracks) and a somewhat lower energy (2.9 Mev). In a similar experiment, Hincks & Millar (84) could not observe these α-tracks and set a higher value for the minimum half-life. Because of the long exposures necessary for this measurement, further confirmation of one of the experiments should be awaited before choosing between these results.

An unstable isotope of vanadium.—A new isotope, V^{50}, has been found in 0.24 per cent abundance in the mass spectrum of vanadium by Hess & Inghram (85) and by Leland (86). This odd-odd nuclide takes its place among the other long-lived odd-odd species which exist in nature, K^{40}, La^{138}, Lu^{176}. The decay period has not yet been measured, but a lower limit of 10^{12} years has been set by Cohen (87). The mass of V^{50} has been determined by the doublet method and compared with its stable isobars Ti^{50} and Cr^{50}. It is unstable by 1.2 Mev with respect to β^--emission and by 2.39 Mev with respect to electron capture. The first two excited states for Ti^{50} are probably at 1.58 and 3.0 Mev according to the measurements of Pieper (88) and from the systematics of energy levels of even-even nuclei (25) it can be deduced that those of Cr^{50} are not much different. Therefore V^{50} can decay only to the ground states of its isobars or their first excited states at best. The spin of V^{50} has been measured to be 6 (89, 90) and since the ground state and first excited states of even-even nuclei are respectively $0+$ and $2+$ the extremely long half-life of V^{50} is readily explained.

Artificially produced isomers of natural products.—The nonappearance of an energetically possible decay process is of general interest in view of its implications on selection rules in radioactive decay. The two isomers of natural products mentioned here have been produced artificially and there is no evidence for their formation in the natural decay series.

One of these is a short-lived isomer (0.8 sec.) of stable Pb^{207}, the end product of the actinium series. It has been produced by activation of lead with neutrons (91, 92) and by the decay of Bi^{207} (93) which is itself artificially produced. This isomer of Pb^{207} lies 1.6 Mev above the ground state and has been assigned the high spin value 13/2 (13). It is probably not attainable energetically from the β^--decay of AcC″ (Tl^{207}) and the formation of this state from the α-decay of AcC′ (Po^{211}) is too rare for detection (93).

An isomer of RaE (Bi^{210}) can be prepared by neutron irradiation of bismuth (94). It is a long-lived α-emitter (94) with a half-life of about 10^6 years (95) and also decays to the extent of $\sim$0.4 per cent by β^--emission (96). The

interesting point in the present connection is that this long-lived isomer probably represents a lower energy state than RaE and yet it could not be detected in the decay of RaD (Pb^{210}) (96). The extremely long lifetime deduced for this transition is explained by a spin of at least 4 for this isomer. Using independent particle model calculations, Pryce (97) has shown that close lying states of widely different spin are expected for this nucleus.

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RADIATION CHEMISTRY[1]

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Past reviews in these volumes have dealt with the primary physical and chemical phenomena associated with energy loss by ionizing radiations in gases, liquids, and solids [Burton (1); Dainton & Collinson (2); Allen (3); Weiss (4)]. Emphasis in the current review will be directed toward new work and its significance to the general field of radiation chemistry.

Two conferences were held during 1953. The Iowa City Meeting of the Radiation Research Society contained symposia on physical measurements in radiobiology and on the radiation chemistry of aqueous solutions. A Gordon Conference on Radiation Chemistry was devoted to such topics as theory of radiation-induced reactions, radiation chemistry of gases, organic liquids, aqueous solutions, ice, hot atom reactions, food and drug sterilization, and the industrial future of radiation chemistry. The papers presented at the Radiation Research Society Symposium on Aqueous Solutions will be published early in 1954 and those of Allen (5), Hart (6), Dewhurst, Samuel & Magee (7), and Garrison, Weeks & Haymond (8) are covered in the present report.

GASES

Relatively few chemical reactions produced by ionization processes in gases have been studied. This important field of radiation chemistry should be most fruitful in providing information regarding the number of molecules dissociated by excitation without ionization and the number dissociated by ionization. Cage effects, common in liquids and solids, are absent in gaseous reactions and for this reason primary radical recombination reactions occurring along the track of ionizing particles in liquids are eliminated. It is important, therefore, to distinguish between reactions induced by excitation and ionization and to obtain yields of gas phase reactions for dissociation and ionization processes.

To the extent that the gas reactions are initiated by free radicals, photochemical and radiation effects are similar. Fricke (9) has pointed out the correspondence between the chemical effects of α-rays and light of short wavelengths.

Recent work by Jesse & Sadauskis (10) on Po^{210} α-particle ionization in mixtures of noble gases indicates that the absolute value of W, the average energy required to produce an ion pair in various gases, is highly sensitive

[1] The survey of literature pertaining to this review was concluded in January, 1954.

[2] I should like to thank Miss P. Walsh for her assistance in the preparation of this manuscript.

to impurity gases. W for the purest helium used was found to be 41.3 ev/ion pair, whereas, helium contaminated with 0.13 per cent argon gave a value of 29.7 ev/ion pair, near the value of 30 commonly reported in the literature. Likewise, neon with $W = 36.3$ ev/ion pair was reduced to 26.1 upon the addition of 0.13 per cent argon. Similar effects were observed on γ-ray irradiation. It is suggested that the transfer of energy from the metastable states in helium takes place when an excited atom of helium collides with an argon atom. In this process, the argon atom is ionized. Krypton and carbon dioxide, as contaminants, increase ionization in helium but no increase is found when neon is added to helium. This latter observation is understandable since the ionization potential of neon (21.5 ev) is higher than the energy available from the metastable state of helium (19.8 ev). The consequences of transfer of excitation energy from one molecule to another in radiation chemistry have already been discussed by Lind (11) and Manion & Burton (12).

The nature and theory of ionization processes occurring in molecular gases on electron impact are treated by Hagstrum (13). He also measured appearance potentials and the initial kinetic energy of ions formed in the ionization of carbon monoxide, nitrogen, nitric oxide, and oxygen. Foner & Hudson (14) have made progress in employing molecular beam techniques to the detection of atoms and radicals in flames by mass spectroscopy. Since ionization potentials of radicals and atoms are lower than the corresponding appearance potentials of electron dissociation products, their presence in molecular beams can be determined by appearance potential measurements. The difference in appearance potential of radicals and parent molecules is approximately equal to the dissociation energy of the molecule. In the hydrogen-oxygen flame, hydrogen atoms, oxygen atoms, and hydroxyl radicals were positively identified. A search was made for the hydroperoxy radical, a commonly proposed intermediate in radiation and photochemical reactions. At low and high electron energies and low and high pressures in the burning flame, no evidence for this radical could be procured. The methyl radical as well as acetylene, carbon monoxide, formaldehyde or ethane, methyl alcohol, and C_4H_2 were identified in the methane-oxygen flame. The data suggest that C_3H_4, C_3H_6, and C_3H_8 are also present.

Dorfman & Mattraw (15) studied the tritium β-ray-initiated, hydrogen-tritium exchange reaction at room temperature over a pressure range of 59.0 to 399.9 mm. with tritium pressures between 32.2 and 147.7 mm. The initial rate of formation of hydrogen tritide is directly proportional to the product of the pressure and square root of absorbed intensity. A chain exchange reaction occurs having yields expressed in units of G[3] as high as 450 molecules hydrogen tritide per 100 ev. A mechanism is proposed wherein the hydrogen and tritium atoms react with tritium and hydrogen, respectively, forming hydrogen tritide. Termination is by atom-atom interactions presumably at a

[3] G, the yield, is expressed in units of molecules or ions formed per 100 ev of absorbed energy.

triple collision. The results are similar to those reported by Mund and associates (16) on the radon-induced exchange of hydrogen and deuterium.

The decomposition of methane, and of blends of methane with hydrogen, deuterium, methane-d_4, ethylene, and ethane in an electrical discharge was studied by Wiener & Burton (17). Hydrogen and acetylene are the major products in the methane decomposition but ethane and ethylene are also formed as minor constituents. G for methane decomposition depends on the current and voltage but varies from 2.0 to 8.1. Mixtures of methane-deuterium and methane-methane-d_4 show preferential formation of CH_2D_2 with little or no CH_3D formed. A mechanism is suggested in which the methyl radical is the primary radical formed but subsequently becomes excited and CH_2 produced from it is the species present in relatively high concentration. In order to account for the large yields of CH_2D_2, the following reactions were postulated:

$$CH_2 + H_2 \xrightarrow{M} CH_4$$

$$CH_2 + CD_4 \longrightarrow CH_2D_2 + CD_2.$$

Temperatures in the discharge were estimated not to exceed 1100°K. Bretton, Hayward & Shair (18) have investigated the effects of temperature and inert gases on the γ-ray-induced polymerization of acetylene.

LIQUIDS

Water and Aqueous Solutions

Many papers have appeared treating the several phases of the radiation chemistry of aqueous solutions. Significant theoretical and experimental contributions have been made toward an elucidation of the track effects of ionizing radiations in liquid water. Allen (5) and Dewhurst, Samuel & Magee (7) have made critical detailed surveys of the evidence, consistent in experiment and theory, testing the existence of proposed radiation reactions and mechanisms.

Radiation chemists have postulated that ionizing radiations produce hydrogen and hydroxyl free radicals distributed along the track in such a manner that the hydroxyl radicals lie close to the path of the original particle. Much speculation regarding the initial location of the hydrogen atom has been made but it is generally supposed to lie between a few Å and up to several hundred Å away from the site of the electron formation. Hydrogen and hydrogen peroxide, the stable molecular products, coexist with these free radicals. While these products are believed to be formed by pairwise recombination of hydrogen and hydroxyl free radicals, it is possible that they are produced as a result of some molecular dissociation process involving excited water molecules.

Thus, there exists within a relatively small volume an initial distribution of free radicals and molecular products. As these reactive species diffuse from their initial positions, reaction with each other and with solute molecules

occurs. Reactions of the following types lower both free radical and molecular product yields:

$$H + H_2O_2 = OH + H_2O$$
$$OH + H_2 = H_2O + H$$
$$OH + H_2O_2 = HO_2 + H_2O$$
$$H + OH = H_2O.$$

The success of radical pair and molecular product measurements depends on preventing the above reactions from taking place. Chemical systems capable of differentiating between reactions of hydrogen atoms, hydroxyl radicals, and hydrogen and hydrogen peroxide molecules are required for this purpose. Since solute molecules vary in specificity of reaction, it is little wonder that appreciable differences in chemical yields are reported.

Dosimetry.—Chemical dosimetry of ionizing radiations has been an important phase of recent radiation research. Substantially everyone in this field employs aerated ferrous sulfate solutions in 0.8 *N* sulfuric acid for this purpose. To Hugo Fricke goes the credit for the first extensive use and careful calibration of this dosimeter. In spite of improvements in dosimetry and irradiation techniques, Fricke's value of $G_{Fe^{+++}} = 18.2$ obtained for 0.2 Å x-rays remains a fair average value. Burton (19) recently has suggested referring to the aerated ferrous sulfate -0.8 *N* sulfuric acid dosimeter as the "Fricke Dosimeter." This suggestion has my sincere support. The use of 0.8 *N* sulfuric acid has puzzled many radiation chemists. An explanation may be found in a paper by Fricke & Morse (20). The sulfuric acid was added to water in sufficient quantity to raise the gram-electron absorption of the solution to that of air. Thus, it was calculated that the gram-electron absorption of 0.8 *N* sulfuric acid is the same as the gram-electron absorption of air for x-rays from 0.9 to 0.2 Å in wavelength.

Ferrous sulfate dosimetry of x-rays, γ-rays, and electrons has been the subject of recent extensive investigation and controversy. Weiss (4) concluded that the majority of the experimental evidence was in favor of $G_{Fe^{+++}} = 20.6$ [Miller & Wilkenson (21); Hardwick (22); Allen (5)]. Values of $G_{Fe^{+++}}$ between 15.5 (calorimetric) and 20.6 (ionization) have been used frequently in reporting experimental results. Now it appears that the latter ionization value is too high. Miller (23) recently stated that the ionization value could be reduced to 18.0 by applying corrections for geometry, *W*, the energy for ion pair production in air, and stopping power values for polystyrene.

Hochanadel & Ghormley (24) reported $G_{Fe^{+++}} = 15.6 \pm 0.3$ for Co^{60} γ-rays in air-saturated 0.8 *N* sulfuric acid constant in the range 0.8×10^{20} to 8×10^{20} ev/l. min. This value was obtained by careful calorimetric measurements. A $G_{Fe^{+++}} = 16.8 \pm 0.3$ was found for 1.33 Mev Van de Graaff electrons. Davison *et al.* (25) and Lazo, Dewhurst & Burton (19a) have also reported yields for Co^{60} γ-rays obtained by calorimetry. The former authors

report a yield of 20 in agreement with the ionization work, whereas, the latter authors report a yield of 15.8 ± 0.3. It is difficult to explain this large discrepancy between these groups of workers but Davison (26) has stated that, owing to the limited space in their tubular-type source, cavity-type heating employed by others to insure uniform temperature of the calorimeter jacket could not be used in their experiments. Therefore, the cause of the discrepancy may be due to the inadequate control of the heat loss factor. Impurities in the ferrous sulfate solution may have contributed to previously reported high results on ferrous sulfate dosimetry.

Miller (27) found a $G_{Fe^{+++}}$ of 20.3 ± 1.0 for 2 Mev x-rays measured by ionization methods and found that the yield is independent of dose rate up to 58×10^{20} ev/l. min. Hummel & Spinks (28) and Hummel, Van Cleave & Spinks (29) obtained $G_{Fe^{+++}}$ values of 16.8, 15.8 ± 0.2 and 15.7 ± 0.4 for radium γ-rays, Co^{60} γ-rays, and 24.5 Mev peak betatron x-rays, respectively. In the betatron x-rays the radiation was given in 4 μsec. pulses, 180 times/sec. at dose rates in the pulse of 130×10^{20} ev/l. min. Energy calculations are based on an ionization method, Saldick & Allen (30) measured $G_{Fe^{+++}}$ for 1 and 2 Mev cathode rays and after making corrections for back scattering, window absorption, and *bremsstrahlung*, obtained a value of 15.6 ± 0.5. The yield was independent of beam currents at 2 Mev in the range 6×10^{-11} to 7×10^{-7} amp., corresponding to a mean dose rate in the irradiated zone of 0.46×10^{20} to 52×10^{22} ev/l. min. (an efficient stirring device was employed). In the liquid volume receiving the highest intensity electron beam, dose rates of 38×10^{20} to 50×10^{24} ev/l. min. were employed. At this upper value, 2.5 N of radical pairs per minute are generated in the irradiated zone. Efficient reaction of radicals with oxygen and ferrous ions must occur in order to maintain a ferrous ion yield independent of dosage rate.

Minder (31), using a solution of 86.6 mc. Co^{60} as the source of γ-rays, irradiated ferrous sulfate contained in concentric flasks. By the use of known absorption coefficients and constants of the radiation, a calculation of energy absorption was made with the result that $G_{Fe^{+++}} = 14.4 \pm 0.2$. In addition, a measurement for the mixed internal radiations of Rb^{86} (0.154 mc./cc.) and S^{35} (0.0348 mc./cc.) yielded $G = 14.6 \pm 0.3$ in oxygen-saturated solutions and 7.2 ± 0.2 in nitrogen-saturated solutions.

In summary, it appears at present that the range between calorimetric and ionization values for $G_{Fe^{+++}}$ for x-rays, γ-rays, and energetic electrons has been narrowed to 15.6–18.0. Greater reliability is placed on the lower calorimetric value in view of incomplete knowledge regarding data necessary to calculate energy absorption in water from ionization measurements in air.

Hochanadel & Ghormley (24), in agreement with Minder & Liechti (32), reported that the temperature coefficient of oxidation for 1mN ferrous sulfate is negligible between 25° and 65°C. Hardwick (33), on the other hand, found a difference of 4 per cent/10°C. in the range from 10° to 60°C. This difference is difficult to explain unless, as suggested above, organic impurities are present and contribute to the temperature coefficient. In either case,

holding the temperature to 5°C. introduces a maximum error of 2 per cent, whereas, impurities can readily introduce errors as high as 20 per cent.

Rudstam & Svedberg (34), employing Fe^{59} as a tracer dissolved in ferrous sulfate solution before irradiation, estimated that radiation dosages in the range 0 to 100 r could be measured with an accuracy of ± 2 r. After irradiation the ferric ions formed were separated from ferrous ions by extraction of ferric thiocyanate with isoamyl alcohol and the activity of the phases determined with a liquid Geiger-Müller counter tube.

Hardwick (22) and Allen (5) have discussed the effect of energy of the β-particle on $G_{Fe^{+++}}$. The conclusion is that $G_{Fe^{+++}}$ is independent of the average energy of the electron down to energies of about 20 kev. $G_{Fe^{+++}}$ for H^3 β-rays having an energy of 5.86 kev is 12.9 ± 0.2 .This value is calculated from energy measurements on tritium water based on calorimetry [Hardwick (35)] and on gas density determinations of tritium [McDonell & Hart (36)].

Haissinsky & Anta (37) and McDonell & Hart (36) reported $G_{Fe^{+++}}$ for Po^{210} α-rays of 6.0 and 6.25 ± 0.2 confirming the 6.7 to 5.9 range previously given by Miller (38). The more recent work has been carried out with the Po^{210} dissolved in the solution. Lefort (39) obtained a value of 7.5 for air-saturated and 4.0 for air-free ferrous sulfate for radon and its decay products. After correction for the β- and γ-radiation absorbed in solution, the above values for the α-rays became 6.2 and 3.7, respectively. On the basis of present information regarding radical pair yields of Po^{210} radiation the ratio 6.2/3.7 is much higher than would be expected. However, in strong acid solution it is possible that reaction 3 is relatively higher than has been supposed. (See discussion of reaction 3 and Table I in section on free radical and molecular product yields.)

The ferric ion yields of the $B^{10}(n, \alpha)Li^7$ and $Li^6(n, \alpha)H^3$ nuclear disintegration reactions are 4.2 ± 0.4 and 5.2 ± 0.5 as reported by McDonell & Hart (36). Thus, it is seen that $G_{Fe^{+++}}$ continues to decrease as the energy of the particles is decreased from 5.3 Mev for Po^{210} to 2.3 for the Li^7 and He^4 recoil products of boron.

Ehrenberg & Nybom (40) investigated ferrous sulfate dosimetry and reported yields in agreement with those previously published for x-rays. In addition, a yield of 16.9 is calculated for S^{35} β-rays and 20 for 0.5 to 2 Mev protons. The former is reasonable but the value for protons appears to be too high by a factor of perhaps two. It is possible that under the conditions of measurement, the high γ-ray flux at the cyclotron is the principal contributing factor to the yield.

Mechanism of ferrous sulfate oxidation.—New studies have been reported on the mechanism of ferrous sulfate oxidation. Dainton & Sutton (41), by studying the post-irradiation effect in air-free dilute ferrous sulfate solutions, found that the molecular hydrogen peroxide yield is substantially higher than the reported molecular hydrogen yield. The conclusion is reached also that the yield of hydrogen atoms exceeds the yield of hydroxyl radicals. This experimental result has important consequences and enables one to account

for the $G_{Fe^{+++}}$ from experimental measurements of free radical and molecular product yields. Dewhurst (42) investigated the effect of pH in aerated and air-free solutions. The kinetic scheme of Rigg, Stein & Weiss (43) does not lead to an equation in accord with Dewhurst's pH results on initial yields, nor does it predict the behavior of initially added ferric sulfate.

Amphlett (44) has continued his studies on the ferrous-ferric systems. At pH = 2.46, reduction of ferric ion occurs with an initial yield of 15. Studies were also made on the equilibrium ratios, R, of ferric ion to ferrous ion, obtained on oxidation of ferrous sulfate ($R = 3.3$) and also by reduction of ferric sulfate ($R = 11.2$) by Co^{60} γ-rays. The latter value varies with initial ferric ion concentration. The steady-state level on oxidation is less than that obtained on reduction and indicates that the ferrous-ferric couple is not thermodynamically reversible with respect to hydrogen atoms and hydroxyl radicals.

Abel (45) derived an alternative mechanism to that deduced by Rigg, Stein and Weiss in order to explain the dependence of ferric ion yield on pH. In the new mechanism, the hydroxyl radical cherished by radiation chemists, is dispensed with and reduction of the ferric ion by the electron replaces the hydrogen atoms at high pH. While this mechanism predicts the kinetic behavior of the Rigg, Stein and Weiss results, it is inadequate for deriving the $G_{Fe^{+++}}$ for air-free solutions. Since $G_{Fe^{+++}}$ is so well explained on the basis of experimental values of radical production and postulation of H_2^+, it follows that the stoichiometry proposed by Abel yields but one-half the experimental quantities of ferric ion and hydrogen. The clearest evidence for the participation of H_2^+ as an oxidizing species in aqueous oxygen-free ferrous sulfate solutions rests on the experimental fact that two ferric ions and one hydrogen molecule are produced per radical pair (H and OH) formed by the ionizing radiation. The equations are:

$$Fe^{++} + OH = Fe^{+++} + OH^-$$

$$Fe^{++} + H_2^+ = Fe^{+++} + H_2$$

Free radical and molecular product yields of ionizing radiations.—A notable advance has been made by Samuel & Magee (46) in their theoretical treatment of track effects in the radiolysis of liquid water. These authors have constructed diffusion models capable of accounting for the relative amounts of molecular products and free radicals formed by α-, β-, and γ-rays. Hydrogen atoms and hydroxyl radicals are assumed to be formed in pairs at the approximate sites of the original ionizations. Several radical pairs may result from the loss of energy in a single "hot spot." The problem is to determine the fraction of radicals that will escape uncombined and the fraction that will combine in a pairwise fashion to yield hydrogen and hydrogen peroxide as diffusion of the group of radicals into three dimensional space occurs. The experimental distribution of these products in the case of γ-rays is obtained by these authors if they assume that the radical-water molecule collision cross section is $4\pi 10^{-16}$ cm.^{2}, the radical mean free path in liquid water is 10^{-8} cm., the initial radius of the "hot spot" is 3.7 Å and the average

number of radicals per "hot spot" is 2.54. When the radius of the "hot spot" has increased 100-fold, the recombination process is practically complete since adjacent "hot spots" are of the order of 5000 Å apart. The motion of a free electron in liquid water is also discussed. It is concluded that a time of the order of 10^{-13} sec. suffices for the dissipation of the secondary electron's kinetic energy and for its return to the vicinity of the positive ion. Samuel and Magee's calculated ratio of G_2/G_1+G_2 (see below for definition) is 0.23, 0.315, and 0.887 for Co^{60} γ-rays, tritium β-rays, and Po^{210} α-rays, respectively. These ratios are in good agreement with experimental values calculable from Table I.

TABLE I

MOLECULAR PRODUCT AND FREE RADICAL YIELDS* OF IONIZING RADIATIONS IN AQUEOUS SOLUTIONS

Radiation	System	pH	$G_{H_2O_2}$	G_{H_2}	G_1	G_2	G_3	G_{tot}	Ref. No.
23 Mev x-rays	$C_6H_6+O_2$	neut.	—	—	2.74	—	—	—	48
Co^{60} γ-rays	$C_6H_6+O_2$	—	—	—	2.73	—	—	—	48
Co^{60} γ-rays	Fe^{++}	0.5	0.87	0.48	2.86	0.69	0.78	4.33	5
Co^{60} γ-rays	Fe^{++}	0.5	—	0.42	—	—	—	—	23
Co^{60} γ-rays	Br^-	—	—	0.49	—	—	—	—	23
Co^{60} γ-rays	Br^-, O_2	2.9–4.6	—	0.46	2.74	0.92	—	3.66	49
Co^{60} γ-rays	HCOOH	2.7	0.44	0.44	3.00	0.88	—	3.88	6
Co^{60} γ-rays	HCOOH	0.32	0.94	0.23	2.35	0.46	1.42	4.23	50
Co^{60} γ-rays	$Ce^{4+}+CO$	0.5	—	—	2.54	—	—	—	51
Co^{60} γ-rays	$C_6H_6+O_2$	acid	0.58	—	2.6	—	—	—	52
Co^{60} γ-rays	1–22 M H_2O_2	neut.	—	—	—	—	—	9.9	53
Co^{60} γ-rays	Fe^{++}	0.5	—	0.42	—	—	—	—	23
2 Mev x-rays	H_2O_2+KI	—	—	0.60	—	—	—	—	54
2 Mev x-rays	Fe^{++}, Ce^{4+}	0.5	—	0.48	—	—	—	—	54
2 Mev x-rays	$H_2O_2\pm KI$	neut.	—	0.32	—	—	—	—	55
2 Mev x-rays	Lactic acid	acid	0.52	0.52	3.08	1.04	—	4.12	56
0.22 Mev x-rays	$Fe^{++}+O_2$	0.5	0.82	—	—	—	—	—	41
0.22 Mev x-rays	Fe^{++}	0.5	0.62	—	—	—	—	—	41
x-rays	organic	—	—	—	—	—	—	3.6	57
0.1 Mev x-rays	I^-, etc.	—	—	0.49	—	—	—	—	58
x-rays 0.9 Å	Ce^{4+}	0.5	1.8	2.0	—	—	—	10.1	59
H^3 β-rays	HCOOH	2.7	—	0.51	2.35	1.02	—	3.37	6
0.95 Mev Protons	$\pm O_2$	neut.	0.3–2.0	—	—	—	—	—	60
Po^{210} α-rays	HCOOH	0.5	—	1.57	0.43	3.14	—	3.57	6
Po^{210} α-rays	—	acid	1.7	1.8	—	—	—	—	61
Po^{210} α-rays	$Fe^{++}+O_2$	0.5	—	1.62†	—	—	—	—	23
$B^{10}(n, \alpha)Li^{17}$	HCOOH	2.7	—	1.47	0.26	2.94	—	3.20	6

* All x-rays and γ-ray yields have been adjusted to $G_{Fe^{+++}}=15.6$ in as far as possible.

† Assuming $G_{Fe^{+++}}=6.2$.

Dainton & Sutton (41) in work mentioned above made an important contribution in demonstrating that the molecular hydrogen peroxide yield is higher than the molecular hydrogen yield. In essence, this means that a new distribution of radical and molecular products has been found. Let us represent by reaction 1 the net free radicals escaping recombination in stoichiometrically equal numbers and by reaction 3 the excess hydrogen atoms and hydrogen peroxide surviving the net radical recombination reaction 2.

$$H_2O = H + OH \qquad 1.$$

$$H_2O = \tfrac{1}{2}H_2 + \tfrac{1}{2}H_2O_2 \qquad 2.$$

$$H_2O = H + \tfrac{1}{2}H_2O_2. \qquad 3.$$

These reactions are employed only for the purpose of establishing radical and molecular product yields and do not imply that water molecules dissociate directly into the products indicated. Further, let G_1, G_2, and G_3 refer to the yield of water molecules decomposed/100 ev in reactions 1, 2 and 3, respectively. A tabulation of current data reduced to $G_{Fe^{+++}} = 15.6 \pm 0.3$ pertinent to radical pair and molecular product yields is given in Table I. For additional reviews on this subject, see Allen (5, 47), Hardwick (22), and Hart (6).

In general, G_1 decreases and G_2 increases with increasing density of ionization. Another point of interest in Table I is that $G_{H_2O_2}$, the molecular yield of hydrogen peroxide for light particle radiation, increases with increasing acidity whereas G_{H_2} tends to drop. Insufficient work has been carried out on pH effects using other types of radiations to draw any generalizations. Fair agreement is found for values of G_1 and G_2 where these quantities could be deduced from the data.

The total number of water molecules decomposed per 100 ev is given in column 9 of Table I. Except for the work of Lefort & Haissinsky (59) employing the ceric sulfate system and Dainton & Rowbottom (53) G_{tot} equals about 4.0 for γ-rays and x-rays. All systems have been measured in dilute aqueous solution (of the order of 10^{-2} to 10^{-4} M) except that of Dainton and Rowbottom who compared the photochemical and radiation yields on the decomposition of 1–22 M hydrogen peroxide. The value of G obtained depends on the value of the quantum yield for the photolysis of hydrogen peroxide. A quantum yield of 2.0 was used but some uncertainty exists in this quantity since Hunt & Taube (62) report a limiting quantum yield of 0.98 ± 0.05 at 2537 Å at 25°C. If the correct value is 1.0, G_{tot} for the radiation would be 5.0 in fair accord with the remainder of the results. The high value reported by Lefort & Haissinsky (59) may be due to a genuine discrepancy in the experimental results. Johnson & Allen (54) obtain $G_{H_2} = 0.49$ for air-free ceric sulfate, whereas, Lefort and Haissinsky report $G_{H_2} = 2.0$ for the same system. More data is needed on these reactions and particular emphasis should be placed on the pH dependence of the molecular product and radical yields.

The data of Table I illustrates that G_{tot} is substantially independent of ionizing particle employed. Whereas G_1 and G_2 are highly dependent on particle mass and energy, G_{tot} is nearly independent of these parameters. In

the case of γ-rays and β-rays most of the energy is spent in the production of free radicals. Hydrogen and hydrogen peroxide, on the other hand, are the predominant products formed from α-particles and by the recoil atoms from the B^{10} disintegration. If hydrogen atoms and hydroxyl radicals are the primary products formed from water, then conditions for recombination of like radicals are favored by the densely ionizing radiations.

Inorganic solutes.—The radiation chemistry of aqueous solutions containing oxygen and hydrogen peroxide is very complex (4). Sworksi (63) reported results in agreement with those of Ebert & Boag (64) and found $G_{H_2O_2} = 1.26$ in air-saturated 0.8 N sulfuric acid and 0.37 in a helium-saturated solution for light-particle radiation. These yields are substantially lower than those reported by Fricke (65). Shalek & Bonner (60), employing 0.95 Mev protons, found that $G_{H_2O_2}$ is dependent on the rate of energy input. $G_{H_2O_2}$ decreases from 2.0 to 0.3 as the dose rate is varied from 2×10^{16} to 10^{22} ev/cc. sec. The removal of air decreases the yield by a factor of two at the low energy input range.

Hart, Gordon & Hutchison (66) reported a γ-ray-initiated chain conversion of isotopically enriched oxygen to normal dissolved oxygen in alkaline solution. The yield of the reaction increases with pH and concentration of enriched oxygen reaching a G_{O_2} of 500 at pH of 12.9. On the basis of these and earlier results on the water-deuterium exchange reaction, the dissociation of the hydroxyl radical was postulated:

$$OH = O^- + H^+.$$

The chain propagation steps for oxygen exchange are then:

$$O^- + O_2^* = O^{*-} + O_2$$

$$O^{*-} + OH^- = O^- + O^*H^-.$$

From the dependence of yield of normal oxygen on pH, the dissociation constant is estimated to be of the order of 10^{-10}. This excludes any possible participation of O^- as a reducing agent in the reduction of ceric ion in 0.8 N sulfuric acid as postulated by Weiss (67) and Uri (68) in order to explain the results of Lefort & Haissinsky (59).

Forchheimer & Taube (69) have provided evidence for the exchange of oxygen of the hydroxyl radical with oxygen of water by a study of the hydrogen peroxide-ozone chain reaction in aqueous solution. In an experiment cited, enriched oxygen from the water appears as gaseous oxygen following reaction of hydrogen peroxide and ozone, each containing oxygen of normal isotopic content. According to the proposed mechanism, the hydroxyl radical is the chain-carrying, intermediate species exchanging with the water.

Complete oxidation of phosphites in the presence or absence of air is reported by Cottin & Haissinsky (70) in the pH range 3.15 to 10.8. Yields in the air-free solution vary from 3.15 to 2.3 and increase to 20 in the pres-

ence of air. Phosphate and hydrogen are formed in equimolar quantities. Oxidation of the phosphite ion by hydroxyl radicals is proposed in the mechanism.

The action of γ-rays on aqueous solutions of ferrin, ferroin, and *o*-phenanthroline was investigated by Lefort & Pucheault (71, 72). Ferrin, ferric *o*-phenanthroline, in air is reduced and shows an after-effect that is attributed to a reduction by hydrogen peroxide or organic peroxides. No after-effect is observed in the absence of air. Destruction of the organic complex and reduction of the ferric ion is demonstrated. Hart (73) studied the γ-ray-induced oxidation of ferrous ion in the presence of formic acid and oxygen in 0.8 *N* sulfuric acid. Under optimum conditions, up to 42 ferric ions are formed per initiating radical. After consumption of oxgyen in this system, efficient reduction of the ferric ion occurs.

Organic solutes.—Garrison and co-workers (8, 74) have continued work on the irradiation of aqueous acetic acid by 35 Mev α-particles and 18 Mev deuterons. An important consequence of these studies is the proof that processes of synthesis as well as degradation occur in simple aliphatic compounds. The primary nongaseous product is succinic acid which is converted to tricarballylic acid upon further irradiation. Malic, citric, and several additional unidentified acid products were also found. Presumably, these compounds originate in secondary reactions of the $\cdot CH_2COOH$ radical with succinic and tricarballylic acids. The synthesis of high molecular weight compounds is also demonstrated by the decomposition of methanol-C^{14} under the influence of its own radiation (0.155 Mev β-ray). This reaction was studied by Burr & Hess (75). Methane was formed with a yield of 5.4 ± 0.3. Ethylene glycol, glycerol, and erythritol [$CH_2OH(CHOH)_2CH_2OH$] were also found in the ratio 1360/14.9/1.0.

Johnson, Scholes & Weiss (56) have investigated the reactions of aqueous lactic acid as a function of pH in the presence and absence of oxygen. Interpretation of the results in terms of radical and molecular product yields is made. In terms of $G_{Fe^{+++}} = 15.6$, these authors find $G_1 = 3.55$ and $G_2 = 0.60$, somewhat higher but in general agreement with the values reported in Table I. Pyruvic acid and hydrogen peroxide are primary products of the oxygenated irradiations being found with $G_{Py} = 3.0$ and $G_{H_2O_2} = 3.6$. The lactic acid reaction has many of the characteristics of the formic acid radiolysis (76) except that hydrogen peroxide is found in the evacuated solutions. The mechanism proposed for oxygenated solutions appears reasonable. However, their proposed mechanism does not account for the amount of hydrogen observed in air-free acid solutions below pH = 2.0. The reaction of the hydrogen atom with hydrogen of lactic acid to produce molecular hydrogen would provide the observed yield.

The "after-effect" in desoxyribonucleic acid irradiated by x-rays was studied by Daniels. Scholes & Weiss (77) and the formation of labile phos-

phate esters demonstrated by Scholes & Weiss (78). Attack of the radicals on the nucelic acid occurs in the presence and absence of molecular oxygen but the oxygen effect is threefold the oxygen-free effect. The "after-effect" is attributed to a slow thermal hydrolysis of the irradiated ribonucleic acid.

An interesting reaction is the chain decomposition of 1 *M* chloral hydrate studied by Freeman, Van Cleave & Spinks (79). The yield for Co^{60} γ-rays and 23 Mev x-rays is a linear function of the inverse square root of dose rate and of the square root of concentration exactly as is the behavior of hydrogen peroxide (80, 81). The authors demonstrate that the average lifetime of the radicals involved in the rate-determining step of the chain propagation reaction is greater than 0.0055 sec.

Sworski (52) and Freeman, Van Cleave & Spinks (48) made a quantitative study of the reactions involved in the irradiation of aerated aqueous benzene solutions. Based on $G_{Fe^{+++}}=15.6$, these two groups of investigators report $G_{phenol}=2.6$ and 2.7, respectively. In addition, Sworski obtains $G_{H_2O_2}=0.58$ in acidic oxygen-free solution which is equal to the molecular yield. Hydrogen peroxide is not formed in air-free, unbuffered solutions but $G_{phenol}=0.29$ is interpreted as resulting from an equivalent forward reaction.

The kinetics of chlorphenol red decolorization by 120 kev x-rays in dilute aqueous solution were investigated by Weber & Schuler (82). It is estimated that about 25 per cent of the radiation intermediates react in such a way as to decolorize the dye. The susceptibility of the products altered by the radiation to further action of the radicals is about the same as that of the parent molecule. In this sense the dye is "self-protecting." Added thiourea is about one third as reactive as the dye. Mongini & Zimmer (83) reported a yield of 14.7 for the oxidation of indigo carmine by radium γ-rays at a pH of 1.15 in aerated aqueous solutions. Dosage curves are not linear and it is found that the yield decreases with increasing pH. Negligible oxidation occurs in the absence of air indicating that the hydroperoxy radical plays an important role in the decolorization reaction.

Minder & Schoen (84) studied the protection effect of formaldehyde, ethyl alcohol, galactose, and 1,4-dimethyl-7-isopropylazulene on the decolorization of methylene blue. As a protective agent the azulene is tenfold more efficient than the other compounds. The yield for methylene blue decolorization is 0.12. Oxygen and carbon dioxide were found to inhibit the decolorization.

Loiseleur and associates (85 to 88) have investigated the postirradiation effects in aqueous gallic acid and tyrosine solutions. Chemical changes as shown by an increase in optical density occur for several days after irradiation. Small amounts of cupric sulfate act as a catalyst on the secondary effect but not on the primary radiation-induced one. The presence of oxygen is necessary for this postirradiation effect. Reducing agents such as sodium hypophosphate, thiourea, cysteine, and ascorbic acid added after irradiation

decrease the effect. Dyes are formed through the action of x-rays by condensation reactions in the presence of oxygen. As an example, indophenol blue is formed from dimethyl-*p*-phenylenediamine and α-naphthol.

Nonaqueous Liquids

Many and complex are the products formed in the irradiation of the simplest organic liquids whereas hydrogen, oxygen, and hydrogen peroxide are the only products obtained during the radiolysis of water. However, under certain favorable conditions much progress has been made in understanding the effects of light-particle radiations and heavy recoil nuclei on liquid halogen-substituted organic compounds. Of primary theoretical and experimental importance is the ion pair or radical pair yields. These yields are of interest in connection with the distribution of active species along the track of the ionizing particle.

Richards (89) has studied the ionization current produced by a collimated beam of Po α-particles in liquid hexane. It was found that the percentage of ions which could be collected was independent of the angle between the path of the ionizing particle and the direction of the collecting field and was proportional to the logarithm of the field strength. Furthermore, the number of ions collected per unit length of track decreases with decreasing energy of the particle. The experimental results can be explained by assuming that only the ions produced by secondary δ-rays outside the primary track can be collected, and it is estimated that the range of these secondary electrons is about 500 Å. Using δ-rays in excess of 1 kev as contributing to ion current collected, Richards finds agreement between calculated and experimental results. Of particular interest in this connection is the fact that 75 per cent of the expected ion current can be collected for x-rays [Mohler & Taylor (90)] but only 0.2 per cent for α-rays. In aqueous solutions roughly 80 per cent of the water molecules dissociated react as free radicals, whereas, for α-rays 10 to 15 per cent are found. From the above result one would expect this latter number to be much lower.

Roberts & Allen (91) found that stabilized free electrons are not formed in liquid ammonia on irradiation by 2 Mev cathode rays or 2 Mev x-rays. Electrical resistance measurements of the liquid ammonia were made during and after irradiation. It was estimated that 3×10^{-9} *M* alkali metal or free electrons could have been detected by the experimental techniques used.

Diphenylpicrylhydrazyl (DPPH) results.—Chapiro *et al.* (92) have continued work using DPPH as a free radical detector and dosimeter for organic solvents. Studies of the yield were carried out employing γ-rays, and 1.2, 0.19, and 0.037 Mev x-rays. The yield of DPPH molecules decolorized per roentgen varied by a factor of 20 over this range of energies. However, after correction for energy absorption in chloroform it was found that the chemical yield per unit energy absorption is independent of wavelength. A kinetic

study of the reaction has been made and the ratio of rate constants for reaction of radicals with DPPH to recombination of radicals has been measured. It is concluded that free radicals produced by the radiation are not uniformily distributed throughout the medium. Chapiro (93) discussed the distribution of free radicals in chloroform and methyl acetate. By assuming that the ratio of the above-mentioned rate constants is of the order of unity (all species involved are free radicals), the concentration of radiation-produced free radicals can be calculated from the critical concentration of DPPH (concentration required to detect maximum yield). It was found that radical concentrations in the track were 2.7×10^{-5} M for chloroform and 0.8×10^{-5} M for methyl alcohol. The total number of radicals produced is respectively eight and three times greater than the number of ions (94). Aqueous solutions, on the other hand, yield about one radical pair for the absorption of 25–30 ev of energy.

The radiolysis of liquid methyl iodide was studied by Schuler & Hamill (95) and Petry & Schuler (96). G values are reported for several aliphatic iodides, bromides, bromobenzene, and ethylene chloride. Triphenylmethane as an additive showed increased yields of products. Alkali iodides decompose in high yield ($G \sim 4$) to give free iodine and display radiation-induced exchange with radio iodine present during irradiation. Decomposition of the alkyl bromides yield mainly hydrogen bromides. The striking difference between relative decomposition yields of methyl and ethyl iodides by radiolysis and photolysis is pointed out ($G_{MeI}/G_{EtI} = 2.7/4.1$ whereas $\phi(MeI)/\phi(EtI) = 0.016/0.40$) and cited as evidence that reactions involving "hot" radicals must be included in the mechanism in order to account for the observed results. Possible mechanisms are discussed.

Hot atom chemistry.—A branch of radiation chemistry exists where processes other than those of ionization occur. Application to radiation chemistry is, however, pertinent since energy imparted to atoms by electrons or heavy ionizing particles is capable of promoting reaction if sufficient energy is transferred. Recoil energy distributions of product atoms resulting from several nuclear processes have been discussed by Libby (97). For example, in the Br^{79} (n, 5 Mev γ) Br^{80} reaction, the Br^{80} atom receives a recoil energy of 168 ev. This energy is insufficient to ionize particles in its path but is far greater than the energy necessary to break chemical bonds. The Br^{80} (4.4 hr.) nucleus subsequently undergoes isomeric transition to Br^{80} (18 min.) with the ejection of a K electron leading to the emission of x-rays or L electrons. The recoil energy transmitted to the nucleus as a result of these relatively feeble transitions is too low to break chemical bonds. The chemical reactions proceeding from isomeric transitions must therefore be assumed to result from reactions initiated by the positive bromine ion and the conversion electron emitted (98). Owing to the multiplicity of reactions involved, the problems of hot atom chemistry are indeed complex. Willard (99) has

compiled a critical survey of recent work on reactions in liquid, solid, and gas phases initiated by (n, γ), (n, p), (γ, n), and β-decay.

The yields of radioactive CCl_3Br, CCl_2Br_2, and higher boiling compounds resulting from radiative neutron capture and isomeric transition of bromine dissolved in carbon tetrachloride have been measured by Hornig & Willard (100) as a function of bromine concentration. The organic yield for each type of transition decreases very rapidly from about 35 per cent at 0.01 mole per cent bromine to about 20 per cent at 15 mole per cent bromine primarily at the expense of CCl_3Br. After 15 mole per cent of bromine has been added, the yields of organic products decrease almost linearly to zero at 100 per cent bromine. This behavior has led the authors to a method of differentiation between high energy and thermal processes. In liquid media, the chlorine atom, after activation, possesses about 370 ev which will be dissipated by collision with solvent molecules substantially at the site of activation. When the energy has been reduced below a few electron volts, reaction of the radioactive chlorine is possible with the high local concentration of organic and inorganic radicals. If reaction now occurs the atom has entered combination by a high energy process. However, if the activated chlorine atom escapes combination by the high energy process it may diffuse as a thermal atom and recombine with other atoms or radicals formed by the transition. The added bromine acts as a trap for these radioactive chlorine atoms as well as for the organic radicals, thus reducing the probability of the chlorine atom entering organic combination. This explains the reduced organic yield upon addition of bromine to carbon tetrachloride. Since competition over a hundred fold range of bromine concentration is observed, it is inferred that different thermalized chlorine atoms diffuse to regions of different local radical concentrations before combining. Of interest in this connection would be studies on the effect of rate of neutron activation. Further recent work pertinent to this subject is reported by Levey & Willard (101), Chien & Willard (102), Hamill & Williams (103), Williams *et al.* (104), Keneshea & Kahn (105), Ivanoff (106), and Gavoret (107, 108).

Polymerization.—Since the mechanism and kinetics of thermal and photochemical polymerization reactions are so well understood, Dainton (109) first suggested the use of polymerization reactions for estimating the number of free radicals formed in aqueous solutions. Subsequently, Dainton & Collinson (2) demonstrated that polymerization reactions can be used to study the effects of track densities. However, these ideas have not been fully exploited. Seitzer, Goeckermann & Tobolsky (110) measured the rates of the Sr^{90}-Y^{90} β-ray-initiated, oil-phase polymerization of styrene, methyl methacrylate, and equimolar mixtures of the two. Their results show that a monoradical, free radical-initiated polymerization occurs with an initiation yield of $G_i = 0.09$ for styrene and 1.1 for methyl methacrylate. In view of the high efficiency for photochemical and thermal free radical initiation, the efficiency

for the radiation-induced initiation must be low. This apparently low initiation yield must be associated with free radical termination along the electron track. For this reason, it would be most important to measure the molecular weight distribution of initial products. These systems were also studied by Ballantine & Manowitz (111) using Co^{60} γ-rays. They report that the effect of dose rate on polymerization requires more study but that their data support a dependence on first power of the dose rate in conflict with the the one-half power dependence reported by Chapiro *et al.* (112). Studies on the γ-ray-induced polymerization of acrylonitrile monomer have been made by Berstein and co-workers (113) and on the depolymerization of polymethacrylic acid in aqueous solution by Alexander & Fox (114).

SOLIDS

The nature of damage produced by the irradiation of solids depends on the nature of the solid and the particle. Damage in metals and semiconductors is caused by energetic, heavy-particle radiations such as neutrons, protons, deuterons, α-particles, and fission fragments. Under these conditions, damage is due solely to the displacement of atoms from lattice to interstitial positions by knock-on collisions. Ionization processes in these solids do not produce damage since the ionized electrons will be able to dissipate their energy very rapidly by electronic conduction. In insulators and ionic solids, damage by ionization processes may be very extensive and result in electron displacements from one covalent bond to another. New chemical compounds result from these electron transfers. Damage by recoil nuclei having insufficient energy to cause ionization may disrupt valence bonds but it is difficult to differentiate between these processes and those caused by ionization. Platzman (115) surveyed the various mechanisms for the conversion of γ-ray energy to heat and concludes that in dielectric crystals electronic excitation of the molecular groups, followed by dissociation and recombination, and ionization followed by recombination are to a large extent responsible for energy dissipation. Since recombination reactions require some activation energy it is suggested that at temperatures below 1°K the recombination reactions are completely inhibited. This part of the energy is estimated as 20 to 70 per cent and is lost as far as heating is concerned.

Ice.—Smaller & Matheson (116) observed paramagnetic resonance absorption corresponding to two species in ice irradiated with Co^{60} γ-rays at liquid nitrogen temperatures. Comparison of irradiated light and heavy water shows that the electrons involved in the transitions are trapped near protons or deuterons, respectively. The data can be explained by assuming that the paramagnetic species are H and OH (or D and OD). This is the first direct evidence for the existence of these species in irradiated ice. Studies on the annealing of the species have been made. Ammonia irradiated at liquid nitrogen temperatures also shows the presence of paramagnetic species, probably H and NH_2.

Ionic solids.—Hacskaylo *et al.* (117, 118) reported that free sodium and free chlorine occur in sodium chloride crystals containing color centers. Free sodium atoms were determined by dissolving the irradiated crystals in an aqueous solution and measuring the pH change. It was found that an aqueous solution of the irradiated crystal was more basic than one made from the unirradiated crystal. The coloration produced by the reaction of chlorine atom with *o*-toluidine was used as a measure of the chlorine atoms present in the irradiated crystals. Since this color results from an oxidation of the *o*-toluidine by chlorine, the presence of free sodium does not contribute to the color produced.

McCallum & Maddock (119) have studied the chemical effects of thermal neutron capture in crystalline permanganates. Damage in these cases is usually attributed to recoil energy given to the manganese atom by the radiating γ-ray quanta. However, it is possible that internal conversion could lead to molecular disintegration as is found in the case of liquid alkyl bromides. "Retention," defined as the fraction of total activity found after irradiation in the same chemical form as the original compound, and the problems associated with its measurement are treated. In the alkali series studied, retention varied from 8.8 per cent for lithium permanganate to 22.5 per cent for potassium permanganate. Hydrates show less retention. The possible mechanisms of retention are discussed in some detail. Chemical reaction of recoil atoms from the n, γ process in rhenium salts is reported by Herr (120).

The amounts of inactive bromine and recoverable 35.9 hr. Br^{82} were measured on pile-irradiated crystalline potassium bromate by Boyd, Cobble & Wexler (121). While the recoil energy of the bromine atom from the (n, γ) reaction may knock it out of its lattice position, it is shown that many nonradioactive bromine isotopes are also released presumably by the γ-rays generated in the reactor or sample. These nonradioactive species lower the specific activity of the bromine in the sample. However, it was shown that a 22,000-fold enrichment was obtained during short irradiations. The retention of Br^{82} increased with time of irradiation suggesting a radiation-induced recombination reaction.

Hennig, Lees & Matheson (122) measured gas yield on sodium nitrate ($G=0.3$), potassium nitrate ($G=0.8$), and potassium chlorate ($G=2.0$–3.0) crystals irradiated by mixed neutron and γ-ray radiations of the Argonne Heavy Water Reactor. The yields are based on energy absorption from the γ-ray flux, fast neutron flux, the betas from Na^{24}, K^{42}, Cl^{38}, and recoils from the $N^{14}(n, p)C^{14}$ reaction. Paramagnetism of the irradiated crystals demonstrated that the oxygen found on melting or on solution of the crystals in water existed in the molecular state in pockets of the irradiated nitrate crystals. Oxygen and nitrite are formed in equivalent amounts. The yields observed with 49 kev x-rays on irradiation of sodium nitrate crystals is similar to that found for pile irradiation. This result suggests that most of the

decomposition originates from electronic ionization and excitation and not from elastic collision of the photoelectrons with the atoms of the molecule. Heal (123) studied the decomposition of sodium azide by 50 kv. x-rays at temperatures of 51° and 102°C. and found yields for the number of azide molecules decomposed per 100 ev of 4.0 and 5.2 respectively. Yields of nitrogen gas, ammonia, and hydroxyl ion were measured after solution of the irradiated crystals in water. Probable mechanisms are discussed. Bowden & Singh (124) observed that silver acetylide exploded when irradiated with 75 kv. electrons at 200 μamp. However, this effect was ascribed to bulk heating of the crystal to temperatures of over 334°C. This conclusion is reasonable since the minimum size of the hot spot necessary for thermal explosion is known to be of the order of 10^{-3} to 10^{-4} cm. diameter at temperatures of 400 to 500°C. Neutron irradiation of cadmium azide, lead azide, silver azide, lithium azide, and silver acetylide with slow neutrons at a flux of 10^{8} n/cm.^{2} sec. failed to cause explosion although it did promote the subsequent course of the thermal decomposition. Crystals of lead azide and cadmium azide were mixed with uranium oxide and irradiated with slow neutrons. Again, no explosion occurred even when the crystals were heated to 290°C. during irradiation. The range of these fission particles in lead azide is estimated at 10^{-3} cm. By assuming that the kinetic energy of the fission recoils heats its cylindrical path to 400°C., it is estimated that this cylinder would have diameter of 200 Å. Apparently, the fission recoils do not promote an exothermic chain decomposition of the explosives sufficient to attain the temperature necessary for "hot spot" initiation. The long, threadlike track of the fission recoils would be likely to dissipate heat too rapidly by thermal conduction.

Polymers.—Crosslinking as well as scission of polymers has been observed. Up to the present time, many of the observations have been of a qualitative nature, merely testing the relative stability of polymers or vulcanized rubbers. Potentially, studies on crosslinking and degradation reactions in polymers could provide valuable data regarding track diameters and densities.

Wall & Magat (125) studied the effects of exposure of solid polymers to pile radiations and the degradation of solutions on exposure to Ra γ-rays. According to the type of polymer, the intrinsic viscosity can be modified by dissolving the irradiated polymer in solvents containing inhibitors. This is evidence that the irradiated solid polymer contains immobilized free radicals. Oxygen is necessary for the scission reactions when solutions of high polymers are irradiated. Charlesby (126) and Charlesby & Rose (127) studied the effect of pile radiations on a number of polymers. Polymethyl methacrylate and polytetrafluorethylene, unlike many other polymers, are found to be degraded by ionizing radiations. Gas formation originating in decomposition of the side chains is observed in irradiated polymethyl methacrylate. Carbon tetrafluoride is found as a decomposition product of polytetrafluor-

ethylene and in this polymer degradation is ascribed largely to scission of carbon-carbon bonds. Stress-strain, hardness, and compression set changes in polyethylene, Nylon, Koroseal, Buna N, neoprene, natural rubber, and Thiokol are given by Ryan (128) as a result of six months exposure to 10^{11} γ/cm.^{2} sec. Extensive crosslinking of these polymers occurs during irradiation although processes of depolymerization and polymerization could contribute to the degradation processes.

Irradiation of cellulose with high voltage cathode rays leads to depolymerization, reduction in crystallinity, and extensive decomposition at dosages of 5×10^8 rep as reported by Saeman, Millett & Lawton (129). Random depolymerization and decomposition of cellulose, both in the easily hydolyzed or amorphous areas and the resistant or crystalline areas result from the irradiation. The rate of hydrolysis of cellulose is greatly increased by irradiation and with this increased rate there is an increase in sugar yield.

IRRADIATION SOURCES AND INDUSTRIAL APPLICATIONS

A wide variety of radiation sources providing particles ranging in energy from the 5.69 kev β-particle of tritium to high energy electrons, protons, deuterons, and α-particles obtained from accelerators have been in general use for radiation chemistry studies. Nuclear reactors, too, have been useful in providing an intense γ-ray flux and thermal neutrons for $B^{10}(n, \alpha)Li^7$, $Li^6(n, \alpha)H^3$ and $Br^{79}(n, \gamma)Br^{80}$ nulcear reactions. Cobalt-60 irradiation chambers have proved to be the most popular radiation source developed within recent years and they are worthy of brief mention in this review.

Radioactive cobalt-60 has risen to prominence as an irradiation source for chemical and biological studies owing to its relative abundance, low cost, and reliable performance, Green *et al.* (130) discuss production problems and cost data for fourteen radioactive isotopes. Cobalt-60, it is concluded, costs about 50 per cent of that for alternative pile-produced isotopes and will compete with fission product sources for a considerable time.

Irradiation chambers designed for chemical research employing Co^{60} have been described by Ghormley & Hochanadel (131); Greenfield, Silverman & Dickenson (132); Blomgren, Hart & Markheim (133); Firestone & Willard (134); and Manowitz (135). In general, the design adopted by a particular laboratory depends on the type of research under consideration but the factors of safety, ease of operation, and reproducible geometry are usually stressed.

These small irradiation chambers are perhaps the modest forerunners of future industrial irradiation chambers utilizing kilocuries of cobalt or fission product radioactivity. Manowitz (136) has presented discussions regarding the feasibility of utilizing fission products in large scale gamma ray irradiators with special emphasis on polymerization possibilities. Since the rate of free radical production is essentially independent of temperature of

irradiation, radiation-induced reactions should proceed at temperatures where thermally-induced free radical production is not feasible. Crean and associates (137) have discussed the application of isotopic sources to food and drug sterilization.

Foster, Dewey & Gale (138) presented the case for Van de Graaff accelerators for sterilization use. Within the maximum voltage range (6 to 8 Mev) of Van de Graaff generators, it is concluded that the cost of obtaining high volume industrial processing does not appear to be excessive.

Industrial applications of photochemistry have been most meager. Perhaps a brighter industrial future is in store for radiation chemistry.

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THEORY OF MOLECULAR STRUCTURE AND SPECTRA[1]

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Until a few years ago, the history of the application of wave mechanics to the structure of molecules and the interpretation of spectra was, broadly speaking, as follows. Very soon after the original treatment of the H atom, quantitative, successful treatments of the H_2 molecule were made. Then, with hardly a gap in time, came qualitative formulation of the orbitals, configurations, states, and spectroscopic transitions possible for diatomic molecules. One might have thought that the logical development to follow would be (*a*) quantitative treatment of various many-electron diatomic molecules; (*b*) qualitative treatment of the spectra of triatomic and tetratomic molecules; (*c*) quantitative treatment of the spectra of triatomic and tetratomic molecules. It is an historical curiosity, however, that (with a few outstanding exceptions such as the work of Pauling on the theory of directed valency and Mulliken's qualitative work on the orbitals and spectra of small molecules) theoreticians jumped these steps and passed straight from a consideration of the H_2 molecule to a class of very much larger molecules, namely, conjugated organic compounds such as butadiene, benzene, etc. There were good reasons for this, of course. In the first place, in contrast to the formidable mathematical difficulty of an exact treatment of any molecule more complicated than H_2, it was mathematically rather simple to explain the bond lengths and spectra of conjugated molecules by considering only their π electrons. Secondly, chemists in the nineteen thirties had a great interest (stimulated, in part, by the economic importance of polymerization processes) in the properties of conjugated compounds. Doubtless, too, the accumulation of precise values of C—C bond lengths in conjugated compounds, as determined by x-ray diffraction, was both a cause and a result of the large volume of theoretical work on the bond lengths of conjugated systems.

As a result of these various influences, the theory of molecular structure developed in a somewhat unbalanced way, becoming unduly synonymous with the theory of organic chemistry, especially the theory of conjugated carbon compounds. During the last few years, there has been an outstanding trend which, on the one hand, has tended to redress the imbalance, although on the other, it has resulted in a new spate of papers on conjugated carbon compounds. The trend referred to has been the return to a consideration of electrons in the simplest systems. A main purpose has been to express their wave functions in new ways such that their properties can be readily

[1] The survey of the literature pertaining to this review was concluded in December, 1953.

visualized. During the year under review, for example, there has been a revived interest in the H_2^+ and H_2 molecules, especially in their excited states. The phrase "simplest systems," however, should be taken to include not only such molecules as H_2 but also simpler models of large molecules such as conjugated carbon compounds. The commonest of these simpler models has been that of the so-called free electron theory, which applies to the electrons of conjugated molecules the well-known "particle in a box" theorem of wave mechanics. 1953 has produced a remarkable number of papers on this theme.

Associated, both as cause and effect, with the trend to reconsider small molecules, is a second trend, namely the development of the theoretical structure of the molecular orbital (MO) approximation for treating molecular problems. A consequence of the two trends has been the appearance, especially in 1953, of a number of papers dealing quantitatively with the structures of many-electron diatomic molecules.

A further feature of 1953, tending to restore the balance of theory, has been the appearance of papers dealing qualitatively with orbitals, shapes, and spectra of triatomic and tetratomic molecules.

Briefly then, the outstanding features of the recent literature have been (*a*) the return to consideration of small molecules, especially in their excited states, and (*b*) development of the free electron theory of conjugated molecules. It will be convenient to divide our detailed review into (*i*) diatomic molecules, (*ii*) molecules containing from 3 to 6 atoms, and (*iii*) conjugated organic molecules.

Diatomic molecules: 1- and 2-electron molecules.—If H_2^+ is regarded as a united atom, the problem of finding the wave functions and energies of its single electron is exactly the same as for a hydrogen-like atom. If one proton is then removed a short way from the other, the wave functions and energies are perturbed. Matsen (1) has used first order perturbation theory to obtain expressions for the energies which then result, in terms of the internuclear distance and charge Z considered to be on the united atom. The true united atom would have $Z=2$. The use of this value of Z, however, gives disagreement with the older, more exact, energy calculations of Teller (2) and Chakravarty (3) [which use as wave function a linear combination of atomic orbitals (AO's) centered on the nuclei] except at extremely small nuclear separations. Matsen therefore uses that value of Z which minimizes the energy of a state. This gives quite good agreement with the older calculations. The treatment is applied to the $1s\sigma$ (ground), $2p\sigma$, $2p\pi$, $3d\pi$, and $3d\delta$ states, the energy being minimized separately for each state. One would expect the treatment to be better for excited states than for the ground state, since the nuclei may more justifiably be regarded as united when the electronic orbital is large. The results show the expectation to be correct.

Hurley & Lennard-Jones (4) have generalized the rigorous equations given earlier by Lennard-Jones & Pople (5) for the energy and wave function of

two electrons in a homonuclear diatomic molecule (e.g., H_2) so that the equations may be applied not only to the ground state but also to excited states. It will be recalled that the essential idea of the earlier work was to express the wave function in terms of the co-ordinates of the two electrons in such a way as to take into account the tendency of the electrons to avoid each other because of their electrostatic repulsion; and that the work was applied to the $^1\Sigma_g^+$ ground state of H_2. Equations now given are appropriate to both singlet and triplet states of various symmetries. In further work, Hurley (6) has expanded the exact wave functions as sums of products of 1-electron functions, i.e., functions in each of which the co-ordinates of only 1 electron are involved. Instead of using AO approximations to these component functions as is usually done, he has determined the optimal forms for the functions by use of the calculus of variations. This makes it more difficult to carry out detailed numerical calculations, but the physical interpretation of the wave functions remains as simple as with the usual wave functions based on AO's. The work has been applied in detail to the lowest $^1\Sigma_u^+$ and $^3\Sigma_u^+$ excited states of H_2.

Hurley & Lennard-Jones (7) have also treated the problem of a heteronuclear diatomic molecule containing two paired electrons. The essential feature of their treatment is to express the field of the two unlike nuclei as the sum of two fields, one of which is symmetrical and the other antisymmetrical in the plane midway between the two nuclei. The results of the earlier papers for the wave functions and energies of the two electrons in the symmetrical part of the field are then used as a basis for a perturbation method of calculating the effect of the antisymmetrical part of the field. In a further paper, Hurley (8) has gone on to give illustrative calculations of the bonding energies and dipole moments of polar chemical bonds. Strictly, the treatment applies only to 2-electron molecules; but by not restricting the positive charges on the nuclei to integral values the screening effect of non-bonding electrons in a many-electron molecule may be simulated and the results should be indicative of the qualitative properties of bonds in heteronuclear diatomic molecules. Essentially the same model was used earlier by Cottrell & Sutton (9) to discuss and reconcile the semi-empirical rules of Pauling, Gordy, and Walsh connecting electronegativities, bond polarities, and bond strengths. The difference is that whereas Cottrell and Sutton used the Heitler-London procedure, Hurley uses the more satisfactory wave functions obtained by him and Lennard-Jones. A particularly important result is that (as Pauling first noticed empirically) the bonding energy in a molecule AB is usually greater than the mean value of the bonding energies of the molecules A_2 and B_2; but (in agreement with the earlier conclusion of Cottrell and Sutton) the reason for this is mainly the reduction of the internuclear repulsion energy and so quite different from that supposed by Pauling (namely, ionic-covalent resonance) and taken as the basis for his electronegativity scale.

Many-electron diatomic molecules.—As already noted, until recently there

was little quantitative theoretical work on many-electron diatomic molecules. This was particularly surprising since (*i*) a fairly complete qualitative interpretation of both ground and excited states of diatomic molecules in terms of MO configurations has been well-known for two decades; (*ii*) the spectroscopic data available on internuclear distances, excitation energies and vibration frequencies of diatomic molecules have long been extensive and precise. One might have thought that the large body of experimental data would have been used to develop quantitative semi-empirical theories, just as it was indeed used by Mulliken and others to develop the qualitative theory of diatomic molecule spectra. Among diatomic molecules, O_2 occupies a unique position since, especially as the result of recent work, the information available about its intravalency shell electronic states is more complete than that about any other diatomic molecule except H_2 or He_2. (This is the more remarkable since all but one of the spectroscopic transitions on which the information concerning O_2 is based are forbidden transitions.) The recent work has included the discovery of new $^1\Sigma_u^-$ and $^3\Delta_u$ states (10), and further data on the $^3\Sigma_u^+$ state (11). It is not surprising, therefore, that when quantitative theories of the states of diatomic molecules came, they should be particularly concerned with the O_2 molecule. Two years ago, Moffitt (12) wrote the first of such papers on the excited states of O_2. He found the antisymmetrical MO method to give disappointing results, and as a result proposed a modified method (see Ch. 8, Volume 4, *Annual Review of Physical Chemistry*). By this new method he predicted the positions of the then unknown $^1\Sigma_u^-$ and $^3\Delta_u$ states, predictions which agree quite well with the recent experimental findings. During 1953 two further papers (13, 14) on O_2 have appeared. Fumi & Parr (13) have used a semi-empirical method to calculate the excitation energies of the states arising from the lowest intravalency shell configurations. Their method is essentially one used by Pariser and Parr (see below) for the computation of the energy levels of complex unsaturated molecules. It is a simpler method than that of Moffitt and is indeed devised to give a compromise between high accuracy and minimum labor. It is based on the LCAO MO method. It allows for configuration interaction; but the number of configurations considered is limited to

$$KK(\sigma_g2s)^2(\sigma_u2s)^2(\sigma_g2p)^2(\pi_u2p)^4(\pi_g2p)^2$$

$$KK(\sigma_g2s)^2(\sigma_u2s)^2(\sigma_g2p)^2(\pi_u2p)^3(\pi_g2p)^3$$

and

$$KK(\sigma_g2s)^2(\sigma_u2s)^2(\sigma_g2p)^2(\pi_u2p)^2(\pi_g2p)^4$$

i.e., 6 electrons are distributed in the various possible ways to the 4 intravalency shell π orbitals. The states arising are thus, respectively, $^3\Sigma_g^-$, $^1\Sigma_g^+$, $^1\Delta_g$, $^{3,1}\Sigma_u^+$, $^{3,1}\Sigma_u^-$, $^{3,1}\Delta_u$, $^3\Sigma_g^-$, $^1\Sigma_g^+$, and $^1\Delta_g$. The calculation of the interaction energies is simplified by the neglect of certain quantities, and a certain core parameter is fitted empirically. However, the vertical excitation energies from the ground state to the lowest $^1\Delta_g$ and $^1\Sigma_g^+$ and to the $^3\Sigma_u^+$ and $^3\Sigma_u^-$

states are computed for various internuclear distances from 1.163 to 1.628 Å and agree within 0.2 ev with the "experimental" values obtained by setting up Morse curves for the ground and each of the excited states using the observed r_e, D_e and ω_e values. In agreement with the recent experimental findings, the $^1\Sigma_u^-$ and $^3\Delta_u$ potential curves are placed in that order just below the $^3\Sigma_u^+$ curve. The so-far unobserved $^1\Delta_u$ and $^1\Sigma_u^+$ states are computed to lie in that order above all the other states. It would be difficult to observe such states since transitions to them from the ground state would be very weak and overlain by far stronger transitions. The results are in good accord with those of Moffitt.

Meckler (14) has also treated the O_2 molecule, using as wave functions linear combinations of AO's represented by Gaussians. With such functions, he has taken into account the effect of a large amount of configuration interaction on the energies of the lower-lying states, by keeping only the 1*s* and 2*s* shells filled, i.e., by distributing the remaining 8 electrons in the various possible ways over all 6 of the orbitals arising from the 2*p* atomic levels. This means a far larger number of states is considered. Out of these, a group of 9 states of $^3\Sigma_g^-$ character is set up and the properties of the ground $^3\Sigma_g^-$ state obtained. The results are good; the binding energy is off by 2 per cent, the internuclear distance by 1 per cent and ω_e by 4 per cent. However, the results for the lowest $^1\Sigma_g^+$ state, obtained by setting up a group of 12 states of that character are not so satisfactory.

Mueller (15) has considered, by both the AO and MO approximations and also by his method of intermediate, "semi-localized" orbitals, the energy separating the lowest $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states of the F_2 molecule. 18-electron calculations by the AO and semi-localized orbital methods agree in predicting the $^3\Sigma_u^+$ state to lie 0.309 atomic units above the $^1\Sigma_g^+$; a similar calculation by the MO method gives the two states in the wrong order.

The above work is limited to homonuclear diatomic molecules. Sahni (16) has considered a heteronuclear molecule, namely CO. He has applied to this molecule the self-consistent MO theory developed by Roothaan (17). The interactions of all the electrons in the molecule are considered. The ground state of CO might be written:

$$KK'(\sigma_1)^2(\sigma_2)^2(\pi)_x^2(\pi)_y^2(\sigma_3)^2.$$

The most weakly bound orbital is taken to be σ in type, since the lowest state of CO^+ is known to be $^2\Sigma^+$ and not $^2\Pi$. The KK′ orbitals are considered to be the same as the $1s_O$ and $1s_C$ atomic orbitals, where the suffixes have obvious meaning. Expressing the other MO's as linear combinations of AO's of Slater type, Sahni finds the coefficients that most nearly satisfy Roothaan's equations to be those given in Table I. (The molecular axis is the *z* axis. To express the $2p_z$ contributions, the O nucleus is taken as the origin and OC taken as the positive *z* direction. The $2p_z$ AO's are then taken as positive on the side of increasing *z*. π_y is of course built from $2p_y$ AO's with exactly the same coefficients as for the construction of π_x from $2p_x$ AO's.) Contours of

TABLE I

ORBITALS FOR THE CO MOLECULE

Molecular Orbital	$(2s)_O$	$(2s)_C$	$(2p_\sigma)_O$	$(2p_\sigma)_C$	$(2p_\pi)_O$	$(2p_\pi)_C$	Calculated Energy ev	Observed Ionization Potential ev
σ_1	0.675	0.270	0.231	−0.227	—	—	−43.369	
σ_2	0.7176	−0.4926	−0.6065	0.168	—	—	−20.011	−19.70
π_x	—	—	—	—	0.8145	0.4162	−15.969	−16.58
σ_3	0.187	0.6145	−0.189	0.7626	—	—	−13.373	−14.01

equal electron density are plotted for each of the orbitals. As the table shows, the calculated energies are in agreement with the observed ionization potentials to within about 0.6 ev; and the most weakly bound orbital turns out to be, as it should, of σ type. Of the three σ orbitals, σ_1 lies primarily between the O and C atoms, σ_2 lies primarily on the side of the O remote from the C and σ_3 lies primarily on the side of the C remote from the O. One sees the powerful effect of the exclusion principle in causing the pairs of σ electrons to lie primarily in three separate regions of space. σ_1 is thus a bonding orbital, σ_2 and σ_3 largely non-bonding orbitals. One notes, too, how strongly hybridized are the C valencies contributing to σ_1 and also to σ_3 (cf. the original suggestion of Long & Walsh (18) that this was so). The C valencies in these two orbitals are not so far off the acetylenic condition of equal contributions from the $2s$ and $2p$ orbitals; i.e., one projects strongly towards the O and the other correspondingly projects in the opposite direction. All the orbitals except σ_3 are polar towards the O atom; but the projection of σ_3 keeps the dipole moment of the molecule low. The calculated moment is the difference of two large quantities, but turns out to be 1.00 D with the negative end on the C, which should be compared with the experimental value of 0.118 D of unknown direction. These results are not qualitatively new, since they were all earlier realized by Moffitt (19) from a simpler, semi-empirical treatment; but quantitatively and in the method used they represent a considerable advance. Sahni compares his electron density results with those obtained earlier by Mulligan (20) who applied Roothaan's self-consistent equations to the CO_2 molecule and also considered the interactions of all the electrons present. The total charge density, as integrated over planes through points along the nuclear axes from minus infinity past an O atom as far as the C atom, is almost identical for the two molecules (as it should be since, as Long & Walsh (18) stressed, the CO bond length is very similar in the two molecules); but, of course, differs considerably on the plus infinity side of the C atom. The agreement of the observed and calculated first ionization potentials of CO may be somewhat fortunate, since Mulligan's similar treatment of the CO_2 molecule gave a first ionization potential 2.3 ev too low. The π orbitals of CO are bonding, so that one may say that altogether three bonding orbitals are filled. Whether one says the bond is triple or double depends

upon how one defines a bond. To say that it is triple obscures the fact that the two π orbitals must be only weakly bonding because of their polarity and makes it less obvious why the bonds of CO and CO_2 are so similar [cf. (18)]. Sahni's work applies primarily to the ground state. One would like to see similar calculations for the excited states of CO; Sahni has calculated the energy of the lowest normally-unoccupied orbital ($\bar{\pi}$), but the transition from σ_2 to $\bar{\pi}$ is indicated as needing 20.62 ev, which is much too high.

As part of a program of considering the structures of some simple molecules with lone pair electrons, Duncan & Pople (21a) have also considered a heteronuclear diatomic molecule, namely HF. The main conclusion they stress, on the basis of MO theory, is the probability of a substantial contribution to the dipole moment from the lone pairs on the F atom. In other words, the polarity of the single bonding orbital may be much less than would otherwise be supposed. Kastler (21b) has also considered HF.

Molecules containing from 3 to 6 atoms.—It has now become generally realized that lone pairs frequently make substantial contributions to the total dipole moment of a molecule. Duncan & Pople (21a) have improved the earlier calculations of Pople (22) on this theme for the particular case of the ground state of the H_2O molecule.[2] Their procedure is to use the observed dipole moment to get approximate wave functions for the occupied orbitals and so to discuss the distribution of electron density in the molecule. They use their results to calculate the electric quadrupole moment; and have briefly considered also the NH_3 molecule.

Consideration of isoelectronic molecules is an old and valuable procedure in molecular structure work. The H_2O and NH_3 molecules may be regarded as formed from HF by partial withdrawal of protons from the F nucleus. Similarly, the HNO molecule may be regarded as formed from O_2 by partially withdrawing a proton from one of the O atoms. Orgel (23) has used the idea to obtain a qualitative diagram for the low-lying levels of the HNO molecule. The lowest states of O_2 are, in order, $^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$. If we suppose a proton to be partially withdrawn in such a way that the resulting HNO is linear, we should expect corresponding $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$ states. The intervals between these states would change from their values in O_2 and the distribution of electrons would become unsymmetrical, but the qualitative order of the levels should remain the same. If we now move the proton off the NO axis (since the HNO molecule is expected to be bent in its ground state; see below), the $^1\Delta$ level will be split into two levels which we may label $^1A'$ and $^1A''$ according as the total wave function is symmetric or antisymmetric, respectively, in the plane of the molecule. Of these it is easily seen that $^1A'$ will lie the lower and, for an HNO angle appreciably less than 180°, will come to lie below the $^3A''$ level which corresponds to the $^3\Sigma_g^-$ ground state of O_2. The ground state of HNO is thus expected to be singlet and in it the π

[2] Ellison & Shull (68) have published an important preliminary account of a calculation by Roothaan's self-consistent MO method of the orbital energies in the ground state of the H_2O molecule.

electrons of the original O_2 molecule are expected to occupy orbitals which may be described as

$(a')^2$	$(a'')^2$	$(\bar{a}')^2$,	$^1A'$.
lone pair on O atom	N—O "π" bond	lone pair on N atom	

In other words, the effect of withdrawing the proton from O_2 is to cause the electrons which were originally distributed equally in two planes to become concentrated in one (the molecular) plane. The lowest-energy absorption should then be to the $^3A''$ state corresponding to the O_2 $^3\Sigma_g^-$ state and having the configuration

$$(a')^2 \quad (a'')^2 \quad (\bar{a}')(\bar{a}''),$$

where $\bar{a}''$ is an antibonding N—O "π" orbital. The next lowest-energy absorption should be to the $^1A''$ state having the same configuration and corresponding to the other component of the $^1\Delta_g$ level. Both the lowest-energy transitions may be described as the jump of an electron from a lone pair ("σ") to an antibonding ("π") orbital. At higher energy still, should come transition to the state that corresponds to the $^1\Sigma_g^+$ level of O_2, viz.,

$$(a')^2 \quad (a'')^2 \quad (\bar{a}'')^2, \quad ^1A'$$

but this transition now involves a 2-electron jump.

These ideas are very simple, but they provide the basic qualitative treatment for interpreting the spectra of nitroso compounds. The spectrum of HNO is unknown, but RNO molecules have weak absorption bands (with $\epsilon_{max.}$ *ca.* 10 when R is aliphatic and *ca.* 50 when R is aromatic) which extend from the infrared into the visible and which are responsible for the blue or green colors of the compounds. Lewis and Kasha suggested that these bands were due to a triplet←singlet transition. Orgel suggests they are due to the $^1A'' \leftarrow {}^1A'$ transition. Similarly, Orgel suggests that the near ultraviolet absorption of ClNO (a very broad absorption maximum around 30,000 cm.$^{-1}$ with $\epsilon_{max.} = 32$) is due to the $^1A'' \leftarrow {}^1A'$ transition, though in ClNO, of course, the orbitals must be less localized than in HNO. The weaker absorption of ClNO in the visible region Orgel attributes to the $^3A'' \leftarrow {}^1A'$ transition. If a second proton is withdrawn from the O_2 molecule to form the HNNH molecule, we obtain the prototype of the azo compounds. Orgel suggests that the weak absorption of azomethane at *ca.* 25,000 cm.$^{-1}$ ($\epsilon_{max} = 16$) is due to the analogue of the above $^1A'' \leftarrow {}^1A'$ transition.

Within the year an interesting letter by Reid (24) has appeared on the single-triplet separation to be expected for antibonding "π"←lone pair "σ" transitions. Reid gives various arguments why this separation should be much less than for "π"←"π" transitions; and concludes that it may be only 100 cm.$^{-1}$ or so compared with *ca.* 7,000 cm.$^{-1}$ for "π"←"π" transitions. This conclusion would not agree with Orgel's assignments for ClNO, since the latter imply a singlet-triplet separation of *ca.* 14,000 cm.$^{-1}$ In this connection,

it should be noted that the weak absorption of ClNO in the visible appears to be due, not to a single, but to two electronic systems [see (25)], the separation of these being *ca.* 4,500 cm.$^{-1}$ The interpretation of the ClNO spectrum has also been briefly considered by Walsh (25); but the experimental data are simply not sufficient for any assignments to be definite.

If two protons are partially withdrawn from one atom of the O_2 molecule, we obtain the HCHO molecule. The low-lying levels of formaldehyde should thus be related to the O_2 levels in much the same way as are those of HNO or HNNH. This relation has been considered by Walsh (26). Again the ground state is singlet and corresponds to one of the components of the $^1\Delta_g$ state of O_2. The most weakly bound electrons are in a lone pair (b_2') orbital on the O atom and, as was realized earlier by McMurry and Mulliken, the lowest-energy transition is to the configuration

$$\cdots (b_2')\quad (b_1'')\text{,}\quad A_2\text{,}$$

where b^{1}'' stands for a "π" antibonding CO orbital. The difficulty is to know whether the upper state of the near ultraviolet absorption and fluorescence bands is the singlet or triplet state (corresponding to the $^1A''$ and $^3A''$ states of HNO above) which can arise from this configuration. A detailed discussion is given by Walsh, who concludes that the absorption involves both $^3A_2 \leftarrow {}^1A_1$ and $^1A_2 \leftarrow {}^1A_1$ transitions (and probably other transitions towards shorter wavelengths). It is possible to give an interpretation of the fluorescence bands which represents them as proceeding exclusively from the triplet upper state, but certain difficulties remain. A definite interpretation of these fluorescence bands is important not only for spectroscopic, but also for combustion theory, since during the oxidation of hydrocarbons and their derivatives, the formaldehyde fluorescence spectrum is frequently emitted. A major new point (23) which has to be taken into account in considering the fluorescence and absorption spectra is the possibility that in both the $^3A_2$ and $^1A_2$ states the HCHO molecule is nonplanar. This carries with it the possibility—if the departure from planarity is small—that inversion splitting of some of the vibrational levels in the upper state may be important. The nonplanarity is expected to be more marked in the

$$\cdots (b_2')^0\quad (b_1'')^2\text{,}\quad {}^1A_1$$

state which corresponds to the $^1\Sigma_g^+$ state of O_2 and which could only be reached by a 2-electron jump from the ground state. As a consequence, this state may lie much lower in energy than would otherwise be the case. Walsh (27) has also briefly considered the interpretation of the near ultraviolet absorption spectrum of acetaldehyde. Here, too, at least two electronic transitions are involved. If the longer wavelength (weaker) of these is taken to be the analogue of the formaldehyde $^3A_2 \leftarrow {}^1A_1$, while the other is the analogue of $^1A_2 \leftarrow {}^1A_1$, then the singlet-triplet separation (<800 cm.$^{-1}$) is much less than that of $\pi \leftarrow \pi$ transitions, in agreement with Reid's ideas mentioned

above. However, these two transitions move apart in formaldehyde; the weaker one moves to long wavelengths and the stronger one to short wavelengths, so that the separation would be nearer 6000 cm.$^{-1}$. These opposite shifts offer an interesting problem for the theoretician.

If two electrons are partially withdrawn from each of the O atoms of the O_2 molecule, one obtains the C_2H_4 molecule. This means that the energy states of C_2H_4, like those of HNO and HCO, are related to those of O_2. The relationship, however, is now more distant and some of the low-lying states of C_2H_4 have to be regarded as arising from higher states of O_2 than the lowest $^3\Sigma_g^-$, $^1\Delta_g$ and $^1\Sigma_g^+$ states. The absorption transitions of C_2H_4 that are expected to require the least energy thus do not correspond to the lowest transitions of HNO and HCHO. Put in another way, the most weakly bound electrons of the C_2H_4 ground state lie not in a lone pair but in a b_{3u} or "π" orbital; and the expected lowest-lying transitions are of "π"←"π" rather than "π"←"σ" type. If we represent the lowest-lying excited states by single MO configurations they could be written

$$\cdots (b_{3u}) \quad (b_{2g}), \quad {}^{3,1}B_{1u},$$

where b_{2g} stands for an antibonding "π" orbital, and

$$\cdots (b_{3u})^0 \quad (b_{2g})^2, \quad {}^1A_1g.$$

A 2-electron jump would be required to reach the last-named state from the ground state. Only the $^1B_{1u}$ state may be reached from the ground state by an electronically-allowed transition. During the last few years there have been several attempts to calculate the heights of the lowest excited states above the ground (X^1A_{1g}) state. Moser (28) has now carried out a 4-electron treatment by the antisymmetrical MO approximation. His work is similar to an earlier 2-electron treatment by Parr & Crawford (29) who obtained the vertical transition energies given in Table II. The special feature of the new work is that it takes into account interaction between the various configurations that can be obtained by distributing 4 electrons over the bonding "π", antibonding "π", bonding "σ" and antibonding "σ" C—C orbitals. Moser concludes that the "π"—"σ" interaction is nearly negligible in the ground state and has only a small effect in the excited states; and finds vertical transition energies very similar to those of Parr and Crawford. From the simple MO configurations given above, one would expect the B_{1u} states to lie below the $^1A_{1g}$; the results of Parr and Crawford and of Moser agree with this. Treatments by the valence bond (VB) approximation, however, give an opposite order for the $^1B_{1u}$ and $^1A_{1g}$ excited states. Thus, Craig (30) considered ethylene as a 2-electron problem (allowing for polar canonical structures) by the VB method. The excitation energies found are given in Table II. They refer to a planar upper state, but are not strictly vertical transition energies. Altmann (31) carried out a 12-electron treatment by the VB approximation, finding, like Craig, that the $^1A_{1g}$ excited state should lie below the $^1B_{1u}$ and obtaining the vertical transition energies given in Table II.

TABLE II

TRANSITION ENERGIES FOR C_2H_4

Investigator	Transition		
	$^3B_{1u}\leftarrow X^1A_{1g}$	$^1B_{1u}\leftarrow X^1A_{1g}$	$^1A_{1g}\leftarrow X^1A_{1g}$
Parr & Crawford	3.1	11.5	15.0 ev
Moser (28)	—	11.42	14.74
Pariser & Parr (50a)	2.4, 1.8	10.1, 10.8	12.5, 12.5
Craig	—	8.9	7.8
Altmann	—	13.0	11.7
Moffitt & Scanlan	5.5	7.3	—
Pariser & Parr (50b)	4.5	7.6	—
Moser (33)	6.0	7.2	—

Experimentally, the ethylene absorption spectrum shows (*a*) very weak diffuse bands between 3400 and 2600 Å; (*b*) weak absorption with some diffuse bands from *ca.* 2100 to 1745 Å; (*c*) sharp, intense, pairs of bands extending from 1745 Å to shorter wavelengths; (*d*) a broad, strong, region of continuous absorption with a maximum around 1630 Å. The 3400 to 2600 Å bands are so weak that they have been obtained only with liquid ethylene; they have been variously assigned to the triplet←singlet transition and to a tail of the $^1B_{1u}\leftarrow X^1A_{1g}$ transition, but either assignment is quite unproven. The sharp, intense, pairs of bands from 1745 Å are known to represent the first Rydberg transition of the molecule and therefore probably have the assignment $\cdots(b_{3u})(3s+3s,\ a_{1g})$, $^1B_{3u}\leftarrow X^1A_{1g}$. All workers so far have assigned the 1630 Å maximum to the allowed $^1B_{1u}\leftarrow X^1A_{1g}$ transition, but beyond its high intensity there is no evidence as yet for this. If we accept the assignment, then since 1630 Å corresponds to 7.6 ev, all the theoretical calculations are most disappointing; they give results which are much too high. We have already referred to the fact that Moffitt (12) found the antisymmetrical MO method similarly disappointing when applied to O_2, and in consequence proposed a modified procedure. Moffitt & Scanlan (32) have now applied this modified method to C_2H_4 and have obtained the vertical transition energies given in Table II. Accepting the above assignment of the 1630 Å peak, the energy (7.3 ev) of the $^1B_{1u}\leftarrow X^1A_{1g}$ transition calculated by them is good. Moser (33), following work by Pariser and Parr (see below), has made changes in his procedure of calculation (one being to replace the analytical value of a certain integral by an empirical value) and managed to obtain a transition energy of 7.2 ev. However, the statement of Moffitt and Scanlan that "there is no doubt" that the 1630 Å absorption is due to the $^1B_{1u}\leftarrow X^1A_{1g}$ transition is too strong. One needs to remember that the absorption maximum in question occurs at shorter wavelengths than the first Rydberg transition and could well involve an excited MO constructed from

$3p$ C AO's[3]; there is no certainty at all that its interpretation must be limited to a pure intravalency shell transition.

Regarding the 2100 to 1745 Å absorption, Mulliken has taken the view that it is a tail of the 1630 Å absorption. There is a good deal that can be said against this view. Craig (30) has given a number of cogent arguments against it. Further, the experimental absorption curve is so flat from 2000 to 1770 Å that it does not look probable that the transition can be the same as causes the steeply-descending, long wavelength portion of the 1630 Å peak. However, Moser accepts Mulliken's view and cites some new experimental data which appear to support it. Moffitt and Scanlan interpret the absorption as due to the $^3B_{1u} \leftarrow X^1A_{1g}$ transition, since according to their calculations this transition ought to lie at about 2250 Å. It should be noted that Moffitt and Scanlan, and Moser in his revised calculations, find a singlet-triplet separation much less than that given by the other MO calculations, and much nearer the average experimental value of *ca.* 7,000 cm.$^{-1}$ cited by Reid (24) for "π" $\leftarrow$ "π" transitions. In view of all these discrepant assignments and the absence of any considerable experimental data on the nature of the 2000 to 1770 Å absorption, much further work is obviously required. Incidentally, Altmann interprets the pairs of bands from 1745 Å as due to the two transitions $^1B_{1u} \leftarrow X^1A_{1g}$ and $^1B_{2u} \leftarrow X^1A_{1g}$; but this is in error for it is proven that the separation of the bands in each pair is vibrational and there is no doubt that all the sharp bands are due to the Rydberg transition.

Following work by Mulliken, it has long been recognized that the $^1B_{1u}$ state in its equilibrium form should have one CH_2 plane twisted through 90° relative to the other. Because of this there has been much interest in the twisting frequency of C_2H_4. The antisymmetrical MO treatment gives 995 cm.$^{-1}$ as an upper limit for the frequency in the ground state; which is too low since the experimental value is now thought to be 1027 cm.$^{-1}$. The method of Moffitt and Scanlan, however, yields the satisfactory value of 1158 cm.$^{-1}$ as an upper limit. Walsh (34) has concluded that the twisting should not be the only change of shape in the $^{3,1}B_{1u}$ states; there should also be a pyramidal arrangement of the bonds about each C atom. The MO's that can be constructed for a planar C_2H_4 molecule are qualitatively the same as can be constructed for a planar N_2H_4 molecule; the difference is that in the ground state of the latter an extra orbital is fully occupied that is empty in the ground state of the former. If, therefore, the actual shapes of the C_2H_4 and N_2H_4 ground states differ, the change of shape reveals the effect of placing electrons in the extra orbital. It follows that the shape of the first excited state (singlet or triplet) of C_2H_4 should tend to be that of the ground

[3] The separation of the 1630 and 1745 Å absorptions is similar to that of the benzene 1795 Å and short wavelength part of the 2100 to 1900 Å absorptions. The benzene 1795 Å peak is known to involve a Rydberg transition, probably to an upper orbital constructed from $3p$ atomic orbitals; the short wavelength part of the 2100 to 1900 Å benzene absorption is believed by the reviewer to involve a Rydberg transition to an upper orbital constructed from $3s$ atomic orbitals.

state of N_2H_4. More generally, the first excited state of a molecule containing n electrons can be expected to belong to the same symmetry class as the ground state of a similar molecule containing $n+1$ or $n+2$ electrons. So far as is known, there are no exceptions to this rule; the known shapes of the ground state of NO_2 and the first excited state of CS_2 form an example of its truth. In the ground state of N_2H_4 it is known that (*a*) there is a pyramidal arrangement of the bonds about each N atom; (*b*) one NH_2 group is twisted relative to the other. The shape of the ground state of N_2H_4 may thus be used as evidence for the expected shape of the $^{3,1}B_{1u}$ excited states of C_2H_4.

Perhaps because so much of spectroscopic theory has been concerned with diatomic molecules (which cannot change their shape), the changes of shape that can occur on electronic excitation of any molecule containing 3 or more atoms have not received adequate consideration. Their neglect has probably also been due to the natural preoccupation of theoreticians with vertical transition energies, and perhaps also to the fact that theory has so largely been concerned with large conjugated molecules where the excitation of one electron out of many is unlikely to cause a marked change of shape. From the point of view of interpreting spectra (especially of small molecules), however, it is most important to know the shape of a molecule in both states concerned in a transition. Allied to the neglect of consideration of the shapes of excited molecules, there has been a neglect of the problem of why particular vibrations appear in a particular spectrum. As an example, the vibrational structure of the benzene 2600 Å transition has been known for some time, but no one seems to have tried to explain why numerous unsymmetrical vibrations are aroused. In 1942, Mulliken (35) drew a correlation diagram between the orbitals possible for a bent and a linear AB_2 non-hydride molecule. The curves connecting the correlated orbitals were shown as rising or falling in energy as the apex angle increased, so that it was possible from such a diagram to say whether a given transition was likely to increase or decrease the apex angle. Mulliken's diagram, however, was either empirical or based on unpublished computations. During the past year Walsh has formulated simple principles which can be used to decide whether a given curve rises or falls in energy as the molecular shape is changed; and has applied these principles to plot correlation diagrams for (*i*) AH_2 (36), AB_2 and BAC (25), and HAB (37) triatomic molecules; (*ii*) AH_3 (38), AB_3 (39), HAAH (37), and H_2AB (26) tetratomic molecules; (*iii*) the pentatomic molecule CH_3I (40); (*iv*) C_2H_4 (34); and (very briefly) C_6H_6 (41). For any diagram one considers two possible shapes for a molecule. For each possible shape there will be a set of appropriate symmetry symbols by which the nonlocalized MO's may properly be described. For each shape there will be a certain number of each species of MO which can be obtained by combining the valency shell AO's on each atom. The energy order of the various possible MO's can usually be decided by a mixture of general considerations and empiricism; and, in most cases, has been given earlier by Mulliken. When the molecular shape is changed from one symmetry class to another, the new sym-

metry label to apply to a particular orbital may readily be worked out or taken from standard group theory results. The abscissa of the correlation diagram is some parameter (e.g., BAB angle of an AB_2 molecule) variation of which between two extreme values carries the shape from one symmetry type to the other. On the left-hand ordinate the possible MO's are written down in energy order for one extreme value of the parameter; on the right-hand ordinate the possible MO's are written down in energy order for the other extreme parameter value. Remembering then that curves of the same symmetry species must not cross, the correlation diagram is obtained by joining the lowest orbital on the left to the lowest orbital of appropriate symmetry on the right, and so on. The real problem is to know whether particular curves ought to be drawn as rising or falling in energy as the parameter is varied. The three principles supposed to govern this may be given as follows for the case of a triatomic AH_2 molecule in which the MO's are all built from H 1*s* and A *s* and *p* AO's. Here the extreme values of the apex angle are taken as 90° and 180°: (*i*) The interpretation of the nonlocalized orbitals must be consistent with the localized orbital description of the bent and linear molecules; as one consequence of this, in the 90° molecule the A *s* orbital does not mix with the other orbitals. (*ii*) Whether or not an orbital becomes more tightly bound with change of angle is determined primarily by whether or not it changes from being built from a *p* orbital of A to being built from an *s* orbital of A. (*iii*) If no change of A valencies from which the orbital is built occurs when the angle is changed, the following subsidiary effect determines whether the orbital becomes more or less tightly bound: if the MO is antibonding between the end atoms, it is most tightly bound when they are as far apart as possible (i.e., in the linear molecule). If it is bonding between the end atoms it is most tightly bound when the latter are as near together as possible (i.e., in the 90° molecule). Consider now the application of these principles. In the linear AH_2 molecule, the possible nonlocalized MO's are (in order): σ_g, σ_u, π_u, $\bar{\sigma}_g$, and $\bar{\sigma}_u$. In the bent molecule, the possible MO's are a_1, a_1, b_2, b_1, $\bar{a}_1$, and $\bar{b}_2$. The components from which these orbitals may be built are

Bent Molecule		Linear Molecule	
$1s+1s$, a_1	p_z, a_1	$1s+1s$, σ_g	p_zp_z, π_u
$1s-1s$, b_2	p_y, b_2	$1s-1s$, σ_u	p_y, σ_u
s_A , a_1	p_z, b_1	s_A , σ_g	

The *z* axis is taken as bisecting the HAH angle and in the plane of the bent molecule; the *y* axis parallel to the H···H line. Components of the same species may be mixed, subject to principle (*i*), to form the actual MO's. The orbital σ_g correlates with a_1, σ_u with b_2, and π_u with b_1 and the second-lowest a_1 orbital. In the linear molecule σ_g and σ_u are alone responsible for

binding the H atoms to A. In a localized orbital description of the molecule, the H atoms would be bound to A by pure p valencies of A when $\angle HAH = 90°$ and by both s and p valencies of A when $\angle HAH = 180°$. To be consistent with this, the a_1 orbital with which σ_g correlates is taken to be built from an in-phase combination of $1s+1s$ and p_z in the 90° molecule; whereas σ_g itself can, of course, only be built from a combination of $1s+1s$ and s_A. By principle (*ii*), therefore, the a_1-σ_g orbital is taken as most tightly bound in the linear molecule [the increase in binding energy from the bent to the linear molecule, however, being somewhat offset because of the subsidiary effect (*iii*)]. The b_2-σ_u orbital is built from $1s-1s$ and p_y in both linear and 90° molecules. Principle (*ii*), therefore, does not apply. But, since the orbital is H↔H antibonding, by principle (*iii*) it is taken to be somewhat more tightly bound in the linear molecule. Remembering principle (*i*) and the interpretation of the lowest a_1 orbital, the A valencies concerned in the a_1-π_u orbital must be pure s in the 90° molecule; whereas, in the linear molecule they can only be pure p. By principle (*ii*), therefore, the binding energy decreases markedly from the bent to the linear molecule. The b_1-π_u orbital is built from pure p valencies of A in both bent and linear molecules; and since it is H↔H nonbonding it is taken as unchanged in binding energy from the 90° to 180° molecule. The $\bar{a}_1$-$\bar{\sigma}_g$ orbital is built from an out-of-phase combination of $1s+1s$ and p_z in the 90° molecule but from an out-of-phase combination of $1s+1s$ and s_A in the 90° molecule; by principle (*ii*) it is more tightly bound in the linear molecule. The $\bar{b}_2-\bar{\sigma}_u$, like the $b_2-\sigma_u$, orbital is more tightly bound in the linear molecule because of principle (*iii*). It follows from all this that AH_2 molecules containing up to 4 valency electrons should be linear in their ground states; those containing from 5 to 8 electrons are likely to be bent; and one containing 9 electrons (e.g., H_2F) should have a considerably greater apex angle than one containing 8 electrons. The latter conclusion may have something to do with the hitherto unexplained fact that the FFF angle in polymeric HF is *ca.* 140° with the H atoms on the lines between the F atoms (42).

The three major curves determining the ground state shape of an AH_2 molecule are those of the a_1-σ_g, a_1-π_u and $\bar{a}_1$-$\bar{\sigma}_g$ orbitals. These change in binding energy (up or down) for essentially the same reason. This reason may be expressed (as above) in terms of the hybridization of the valencies of the central atom. It may alternatively be expressed in the following terms [(25); cf. Pople (22)]. When the central atom has on it no lone pair electrons the repulsion of the bond electrons keeps the molecule linear. When the central atom has on it a single pair of lone electrons, the repulsion between these and the bond electrons causes the molecule to bend and the lone pair electrons to lie predominantly on the side of A remote from the bonds. When an extra lone pair of electrons is placed on A, they come to lie on the opposite side of A to the first lone pair; consequently the bond electrons are subject to equal and opposite repulsions so that the molecule becomes linear again. The important point is that the major factor determining the shape of an

AH_2 molecule is the repulsion between the electrons around the central atom A; and only to a very minor extent repulsion between the nuclei of the H atoms.

Similar orbital curves apply, with only slight modifications, to non-hydride AB_2 molecules. They lead to the expectation that such molecules containing up to 16 valency electrons should be linear in their ground state; that the apex angle should show a marked drop on passing to a 17-electron molecule, a further marked drop on passing to an 18-electron molecule, smaller drops on passing to 19- and 20-electron molecules and then should increase again to *ca.* 180° for a 22-electron molecule. All these expectations are confirmed by the experimental data. The remarkable thing is that the apex angle of such a molecule appears to be fixed within quite narrow limits ($\pm$*ca.* 7°) for a fixed number of valency electrons. Similar correlation diagrams for other classes of molecules lead to the following conclusions. For HAB molecules, those containing 10 or less valency electrons should be linear in their ground states, those with 10 to 14 electrons should be bent and those with 16 electrons should be linear again. For HAAH molecules, those with 10 valency electrons should be linear in their ground states, those with 12 electrons should be bent but planar (*cis* and *trans*) and those with 14 electrons should be bent and nonplanar. For AH_3 molecules, those with 6 valency electrons should have planar ground states, those with 7 or 8 should be pyramidal and those with 10 should be approximately planar again. For AB_3, non-hydride molecules, those with 24 valency electrons should have planar ground states, those with 25 or 26 should be pyramidal, and those with 28 electrons should be approximately planar again.

Such correlation diagrams are very useful not only for predicting the shapes of the ground states of molecules but also for interpreting spectra. They enable the low-lying transitions to be formulated—from which we may state the polarization and whether the transition is allowed or forbidden; they suggest the change of shape to be expected when any particular transition occurs, and, in combination with the selection rules, suggest the vibrational structure to be expected in the transition. Thus, a low-, if not the lowest-, lying absorption transition of the HCO radical should be from a bent ground state to a linear upper state. It is pleasing that, since the correlation diagrams were constructed, Ramsay (43) has made the first report of an absorption transition of such radicals and has concluded that the ground state is bent and the upper state is linear. Similarly, the correlation diagram for HAB molecules shows that the lowest absorption transitions of the HNO molecule should be $^{3,1}A'' \leftarrow {}^1A'$; that these transitions should increase the apex angle somewhat and that the 2-electron $^1A' \leftarrow {}^1A'$ transition discussed above should increase the apex angle much more, which conclusions are all implicit also in Orgel's treatment of HNO. Again, the first excited state of the C_2H_2 molecule should be nonlinear. Ingold & King (44) have now found this to be true. Conclusions concerning the first excited states of the H_2CO and C_2H_4 molecules have been mentioned above. Sometimes an excited state of a molecule which has high symmetry in its ground state may be remark-

ably unsymmetrical; methyl iodide provides an example, for, in one excited state the I atom is expected and found to lie off the trigonal axis of symmetry of the CH_3 group.

Ingold & King (44) have, like Walsh, stressed that analysis of electronic transitions of polyatomic molecules has too often been attempted under the preconception that the upper and lower states would have the same shape. They have accomplished a complete analysis of the 2500 to 2100 Å absorption bands of acetylene, showing that the upper state has a singlet, *trans*-bent, shape; with bond lengths and bond angles almost the same as in the ground state of benzene. Their achievement is the more impressive since, so little have changes of shape in electronic transitions been previously considered, they had to develop for themselves the detailed theoretical rules of selection and intensity that would govern transitions of linear C_2H_2 to non-linear, but planar, states. It is sobering to recall that of all the known electronic transitions of all the known polyatomic molecules only two have so far been analyzed in anything like a complete way, viz., the 2600 Å transition of benzene[4] and the 2500 to 2100 Å transition of acetylene. Compared with the task waiting to be accomplished, the achievements of theoreticians thus far in interpreting the electronic spectra of polyatomic molecules are very slight. What is required is a working out, in all their complex details, of the theoretical rules governing the appearance and intensity of both the vibrational and rotational parts of electronic transitions for all possible changes of shape; and the quantitative deduction and interpretation of the shapes, bond lengths and angles in each of the combining states. These are tasks for the theoretician as much as the practical spectroscopist. Most theoreticians have avoided such tasks and have indeed left the only complete spectroscopic analyses so far achieved to a mere organic chemist. It is common to see a theoretical paper on the calculation of vertical transition energies that is excellent up to the last page (except that the results may be in error by anything up to 100 per cent), but which descends almost to puerility when, on the last page, the author comes to consider assignments to observed spectra. So much of the theoretical work on molecular spectra, too, has been concerned with continuous absorption humps, where it is easy but somewhat unprofitable to assign a particular transition—for with such spectra it is difficult for anyone to say one nay. It would be more profitable to tackle spectra that are full of structure, as, e.g., in many triatomic molecule spectra and in the almost virgin field of molecular Rydberg transitions. In such problems one has to keep in mind all sorts of experimental facts, and assign-

[4] The upper state in this transition is said (44) to have exactly the same shape as the ground state. The reason for this statement is that selection rules based on both states having D_{6h} symmetry fit the facts. It is not clear, however, that this means that both states have exactly the same shape. Indeed, from the appearance of numerous unsymmetrical vibrational modes in the transition, one might doubt it (41). The theoretical problem of how big a departure in the upper state from strict D_{6h} symmetry could be permitted without altering the fact that the D_{6h} rules explain the spectrum, has not been tackled.

ments will not be accepted unless they account for all the many observed details of structure.

It is pleasing that during the last few years attention (45, 46) has been turned to a body of experimental data which hitherto was largely neglected, namely molecular ionization potentials (IP's). Hall (47) has continued the work, calculating the IP's of the methyl- and chloro-substituted ethylenes. He assumes values for the first IP's of methane and ethylene, so getting what he calls the methyl- and double bond-group potential parameters. He also assumes first IP's for propylene and 1,1-dimethyl ethylene, so getting a methyl-double bond interaction parameter and a similar parameter for two methyl groups attached to the same C atom. These parameters are used to calculate first IP's for the remaining methyl ethylenes and also higher IP's of all the methyl ethylenes. The difficulty is to test the results adequately, for of the calculated quantities only the first IP's of 1,2-dimethyl ethylene (*cis* and *trans* having closely similar values) and trimethyl ethylene are known. In these two cases the calculated values agree with the experimental to within 0.03ev. Hall similarly assumes first IP's for hydrogen chloride, vinyl chloride, and 1,1-dichloroethylene, so getting respectively a Cl parameter, a Cl-double bond interaction parameter and an interaction parameter for two Cl atoms bonded to the same C atom. He then calculates first IP's for 1,2-dichloroethylene (which, in his approximation, must be the same for the *cis* and *trans* molecules; experimentally they differ by 0.3ev), trichloro- and tetrachloroethylene, and also sundry higher IP's. Unfortunately, there is really no experimental value for tetrachloroethylene and the (tentative) spectroscopic value for trichloroethylene is not in agreement with the electron impact value. The calculated value for 1,2-dichloroethylene is about 0.3ev from the mean of the experimental values for the *cis* and *trans* molecules. It is doubtful, however, whether Hall's calculated values ought to agree with the experimental ones, for he neglects inductive and conjugation effects between CH_3 or Cl groups and the ethylene double bond.

Conjugated organic molecules.—Pople (48) has also reported the results of IP calculations, this time for *s-cis* and *s-trans* butadiene, *s-trans* hexatriene, benzene, naphthalene, and anthracene. He assumes a value for the first IP of ethylene and, allowing for electron interaction effects, calculates first IP's for the other molecules that agree with the experimental values to within ± 0.5ev. The *s-trans* butadiene IP, however, is calculated to be lower than that of the *s-cis*, whereas the IP's of *cis* conjugated dienes generally are lower than those of *trans* and there is some experimental evidence in favor of a lower value for *s-cis* than for *s-trans* butadiene.

Moffitt (49) has used the method he has applied to O_2 and C_2H_4 (see above) to consider conjugated hydrocarbons, especially the allyl radical. Pariser & Parr (50a) have proposed a new semi-empirical method for calculating the wavelength and intensity of the first absorption maximum in the spectra of unsaturated and conjugated molecules. It is based on the antisymmetrical MO method including configuration interaction, but introduces various reasonable approximations and certain empirical elements designed

to reduce the labor in the purely theoretical method and so to make it ultimately applicable to really complex molecules. A preliminary application is naturally made to ethylene and benzene since these molecules have earlier been treated by the more rigorous, nonempirical method; the results are about equally good by the two methods and for ethylene have been quoted (for two variants of the semi-empirical method) in Table II. Having thus established that the new method can give as good results as the anti-symmetrical MO method, Pariser & Parr (50b) apply it to butadiene, pyridine, pyrimidine, pyrazine, *s*-triazine, and also ethylene and benzene; this time adjusting the empirical parameters, not in order to give agreement with those of the more rigorous method, but to duplicate as far as possible the experimental data on the height of the lowest singlet state for each molecule. They obtain good agreement with what is known of the spectra of the compounds (see, e.g., Table II). Pariser (51) has also suggested an improvement in the usual π electron approximation of MO theory, whereby the effect of the σ electrons may be taken into account.

Pariser and Parr stick to the usual LCAO method of approximating MO's. Brown & Matsen (52), following Matsen's work on H_2^+ reported above, write the π MO's of conjugated compounds as linear combinations of united atom orbitals located in each bond of the system. Since the united atom orbital corresponding to the in-phase overlap of two $p\pi$ AO's is also $p\pi$, the treatment is closely analogous to the usual LCAO approximation. Bond orders for various bonds in the ground states of various conjugated molecules are calculated and compared with those of the more conventional theory.

The so-called free electron (FE) approximation represents a more thorough-going attempt to get away from the usual LCAO approximation. The general ideas are described in a review of the earlier work (53). The recent interest in this approximation has been so great that there has been a good deal of overlapping in publications. The most complete work has been that of Ruedenberg & Scherr (54, 55). Probably many teachers of theoretical chemistry have long been in the habit of using FE theory in simple forms as a way of giving students a clear understanding of the basic ideas in the application of wave mechanics to conjugated systems and of how some of the salient facts (such as the shift to long wavelengths of the first absorption system with increasing conjugation) might be qualitatively understood [see, e.g., Walsh (56)]. Until recently, however, the theory has not been generally regarded as more than a useful picture for teaching purposes. Quantitatively, the difficulties have been to know (*a*) what boundary condition to impose upon the wave function at a free end point (i.e., how far does the available space extend beyond the last C atom of a chain), and (*b*) what conditions to impose at a point where the C framework branches. Regarding (*a*), some of the earlier authors (53) have treated the extension allowed for the FE path beyond the last C atom as a parameter to be adjusted to fit experimental data. Ruedenberg and Scherr [cf. Griffith (57); Jaffé (58)] show that the only satisfactory boundary condition for a model consisting

of CC bonds of equal length is that the FE path extends just one bond length beyond the last C atom. As for (*b*), since the electron density must be continuous, at branch points the wave functions in the three branches must (*i*) be equal, (*ii*) obey a condition known as the "conservation condition," involving the first derivatives of the three functions [cf. Griffith (59)]. These conditions were first used by Kuhn but the second had not previously been proven. Various authors (e.g., 57 to 63) have noted a close analogy between the mathematical formulations of the FE and (simplest) LCAO models; Ruedenberg and Scherr now show that this analogy is much more extensive than had previously been realized. Provided the above boundary and joint conditions are imposed, there is indeed an exact parallelism between the results for the two models. Ruedenberg and Scherr establish various theorems. For example [cf. Griffith (59)], the π electron density should be 1 at each C atom joined to only two C neighbors, and $\frac{2}{3}$ at each C atom joined to three C neighbors. Platt (64) has described the construction of a wire model to show how the π electron density in various conjugated molecules varies according to the theorem. Two examples may be mentioned, to show how such a model enables one to visualize the electron density. (*a*) For hexatriene, because of the boundary condition and the need for the density to be continuous and 1 at each C atom, the density in the bonds assumes a wave form that reaches highest values in the end bonds, corresponding to the alternating single and double bonds in the usual formula and to the expectation of most double-bond character in the end bonds. (*b*) For naphthalene, because of the need for the density to be continuous and 1 at atoms 1 to 8, but 2/3 at atoms 9 and 10, the density is particularly low in the 9—10 bond, and highest in the 1—2, 3—4, 5—6, and 7—8 bonds, corresponding to a weak central bond and strong "corner" bonds. Scherr (55) has put features such as these into quantitative form, calculating values of bond densities, bond orders, free valencies, dipole moments and the like. The results are, in general, at least as good as those of the usual LCAO calculations. Fukui, Yonezawa & Nagata (65) have also discussed the reactivities of conjugated molecules, supposing the reactivity to be determined by the density of the electrons in the most weakly bound orbital occupied in the ground state. This idea is particularly plausible since there are several series of reactions [e.g., the inhibiting action of phenyl compounds on gas phase free radical processes (66) and the gas phase reaction of NO_2 with various substances (67)] where the rates are known to correlate with the first ionization potentials of the molecules concerned.

The general conclusion from all this is (as Ruedenberg and Scherr say) that the FE model deserves the same recognition and standing as the simplified LCAO model. Indeed, in some ways the FE model is preferable, notably, in that its assumptions and crudities are the more obvious and that its wave functions are so readily visualized. Of course, the LCAO model has the advantage that it can, in principle, be applied to all the electrons of a molecule, and not merely to the π electrons.

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SPECTROSCOPY[1]

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The present review of Spectroscopy in 1953 will be restricted to discussion of electronic spectra, and will not attempt to cover the very large number of papers on infrared and Raman spectra. The exclusion of the latter may be justified partly by the fact that the preceding (1952) review was confined principally to rotation-vibration spectra and by the expected appearance of comprehensive reviews of these spectra early in 1954.[2] The 1952 literature on electronic spectra has not been covered systematically, but many important papers of that year are included in the present review. This review is restricted further to new measurements and interpretations of spectra, rather than applications of established spectra to chemical analysis, reaction rate measurements, chemical equilibrium, and to other chemical problems. However, it must be recognized that some of these applications have stimulated research in spectroscopy and have suggested new lines of approach to spectroscopic problems. For example, the significant advances made in 1953 on spectra of radicals derived from polyatomic molecules was stimulated largely by photochemical research. It is evident also that identification of functional groups by characteristic spectra, as in organic syntheses, has led frequently to a better understanding of the spectra of complex molecules.

There do not appear to be any major directions in which electronic spectra have advanced during 1953, but moderate advances have been made in many directions. Indeed, the number of directions is so large that classification is difficult. Purely theoretical papers form a class, with a few recognizable subclasses. Experimental papers were classified into those accompanied by interpretations of the data in relation to electronic structure, and those which merely present new data; the latter usually are not discussed. Among the former, some definite classes emerge, which are concerned with atoms, diatomic molecules, polyatomic molecules with ten or less atoms, primary benzene derivatives, larger organic molecules, free radical spectra, and spectra of molecular complexes. Perhaps the most active branches of spectroscopy at present are concerned with microwave spectra and magnetic resonance spectra, which are treated in other chapters of this volume.

[1] The survey of the literature pertaining to this review was completed in December, 1953.

[2] A review by Dr. R. C. Gore, which covers the work done in infrared spectroscopy since his review in Analytical Chemistry (January, 1952), will appear early in 1954. A similar review by Dr. R. F. Stamm will cover the work on Raman Spectroscopy for a similar period. (Private communication from Dr. Gore, December, 1953.)

If any general conclusion can be drawn about the present status of electronic spectra, it can be said safely that experimental progress is still far ahead of theoretical understanding, even for simple molecules. The reason for this situation is not difficult to find. With recent advances in instrumentation, electronic energy levels and intensities may be found quickly and easily for a large number of molecules, even in the vacuum ultraviolet region. But precise and detailed interpretation of positions of energy levels and intensities is, of necessity, a slower process, which leads frequently to complicated mathematical calculations, the results of which cannot be carried over from one molecule to another. The semiempirical approach has the advantage of greater simplicity and generality, but just because of these features it is incapable of explaining the finer details present in the experimental spectra. If this is a correct statement of the present status, it may be expected that the situation will not change in the immediate future, unless there are developments in applied mathematics directed specifically toward shortening the time required for calculations on molecular spectra.

No general reviews on electronic spectra have appeared during the past year. Ultraviolet absorption spectra of steroids have been reviewed by Dorfman (1). A report (2) on far ultraviolet spectroscopy is too incomplete to be generally useful as a guide in this spectral region.

Theoretical Contributions

A series of ten papers by Walsh (3 to 12) is of great value in understanding the general features of spectra of simple polyatomic molecules, as well as the electronic structures of the normal and lower excited states. Walsh correlates the binding energies of electrons in molecular orbitals as a function of some principal molecular angle which determines the over-all shape of the molecule. For example, orbitals and their energies are correlated between linear and bent forms, and between planar and pyramidal forms as limiting cases. Of particular interest is the prediction of change in shape between normal and lowest excited states for some molecules, many examples of which have been confirmed experimentally. Many details of spectra are interpreted, and electronic structure and spectra are predicted for the interesting CH_2 and CH_3 molecules.

A paper which is of fundamental importance to molecular calculations, especially for its point of view, has been published recently by Slater (13). He considers a generalized self-consistent field method, suitable for configuration interaction between any number of states. The best molecular orbitals are not chosen by the usual variational method to make the energy a minimum; sufficient configuration interaction gives the correct answer for any set of orthonormal orbitals. Instead it is required simply that the orbitals be a solution of the Schroedinger equation for the electron moving in the fields of all nuclei and other electrons. It is shown how the potentials and the electronic interactions may be computed in a simple way to meet this requirement, at least in principle. The problem is more tractable if there are

only two nuclei, and the electrostatic potential of the electron field has the full symmetry of the two-center field. Lennard-Jones and co-workers (14 to 18) have shown how to solve the wave equation of this system for two-electron functions. Full use is made of molecular symmetry, and different charges may be present on the two nuclei.

Several interesting nonempirical calculations have been made. The importance of inclusion of interactions between configurations now is well established. Meckler (19) has calculated the energy of two low lying electronic levels in O_2, using all possible configurations which result from eight electrons in twelve $2p$ atomic orbitals, with $1s$ and $2s$ electrons maintained in closed shells. The interactions of nine $^3\Sigma_g^-$ states and of twelve $^1\Sigma_g^+$ states resulting from the configurations were treated. The energy and other properties of the lowest $^3\Sigma_g^-$ state were in good agreement with experiment; calculations on the lowest excited state agreed less well. A less laborious method for O_2 was used by Fumi & Parr (20), who treated a greater variety of excited states with less configuration interaction. Only two $^3\Sigma_g^-$, two $^1\Sigma_g^+$ and two $^1\Delta_g$ states were considered in the interactions, and the other states were represented by single configurations. A number of approximations and some empirical data were introduced. A calculation on HF (21) showed that the interaction of $(1s)_F$ with valence electrons were important. A calculation on the normal and lowest excited states of SF_6, treated as a 12-electron problem, was reported by Duncan (22). A preliminary account of calculations on H_2O, including all electrons, was given by Ellison & Shull (23).

The other theoretical calculations were concerned with the π-electron approximation. However, Ross (24), in a treatment of the lower electronic levels of C_2H_2 included σ-π interactions. The lowest excited state was found to be $^1\Sigma_u^-$ for a linear configuration. This state becomes A_u in a bent (*trans*) configuration, which agrees with the experimental and theoretical conclusions of Ingold & King (25 to 29). A calculation on the π-levels of fulvene by Berthier (30, 31) showed good agreement with normal state, but not with excited state properties. However, the functions derived gave good agreement with experimental intensities. More approximate molecular orbital treatments have been made for a number of aromatic hydrocarbons: polyphenyls, polyenes, and phenylpolyenes by Dewar (32), and of conjugated polyethylenic hydrocarbons by Vroelant (33). Fukasawa (34) computed shifts in absorption spectra of disubstituted benzens.

The nonempirical computations on compounds with multiple bonds usually have neglected the σ-electrons. An analysis of this factor by Pariser & Parr (35, 36) shows that when some of the integrals used in calculation are modified through the introduction of experimental quantities, improved agreement with experiment is obtained. They show also that neglect of exchange terms in expansion of molecular integrals into atomic integrals, compensated by renormalization, gives acceptable values for the two-electron integrals over molecular orbitals, and reduces greatly the labor of computation. The method appears to be promising, especially for large aromatic molecules.

A number of calculations of positions and intensities of electronic transitions have been made recently, based on the free-electron model, for cyanine dyes (37) and other dyes (38, 39). Jaffé (40) developed relationships between free-electron and molecular orbital functions. Simpson (41) pointed out a new use of resonance structures in the theoretical prediction of wavelength shifts on substitution, and in prediction of polarization of electronic transitions.

Experimental Electronic Spectra

An attempt will be made to discuss spectra in order of increasing complexity which is usually, but not always, associated with the size of the molecule. The choice of examples has been difficult, especially in the last parts of this section.

Atomic spectra.—There has been relatively little progress in atomic spectroscopy during 1953, apart from extensions of previously known spectra into the infrared and into the vacuum ultraviolet. There are many interesting applications to astrophysical problems; a comprehensive review of this aspect is needed badly. In this connection should be mentioned solar and other spectra obtained in rocket flights (42); a review of this work was given by Tousey (43). Moore (44) has compiled an ultraviolet multiplet table for 18 elements (atomic numbers 24 through 41). Most of the wavelengths are below 3000 Å. Humphreys (45) discovered the first member of a sixth series in the spectrum of the H atom at 12.37 μ.

Diatomic molecules.—Mention should be made first of an atlas (46) of bands of diatomic molecules observed in emission and in absorption (complete to the summer of 1952). This atlas, prepared under the auspices of the International Union of Pure and Applied Chemistry and the International Union of Astronomy, supplements a previous compilation of data on diatomic molecules (47) published in 1951. Most of the recent work is concerned with extension of existing spectra, some with analysis of previously reported spectra. However, spectra of CN^+ (48), $C^{13}O^{16}$ (49), GeH (50, 51), and RaCl (52) were reported for the first time. In the vacuum ultraviolet Worley (53) found a third series of Rydberg transitions converging to a $^2\Pi$ state of N_2^+. Tanaka (54) found a new spectrum of O_2 in the region 1200 to 1290 Å, and he extended the spectrum of N_2^+ (55) in the vacuum region. Absorption coefficients of O_2 (56) determined by photoelectric methods in the region 1050 to 1900 Å agree with photometric measurements (57) in regions where they could be compared. The latter method was used to obtain absorption coefficients of N_2 (58) between 300 and 1300 Å. Rowlinson & Barrow (59) investigated the absorption spectrum of SiO and GeO from 2000 to 1250 Å and made a vibrational analysis. The spectrum of NO in the vacuum region received considerable attention. High dispersion spectra were obtained by Tanaka (60). Baer & Miescher (61) obtained spectra in the region 2000 to 1200 Å from a discharge in NO partly enriched with N^{15}, and attributed some of the spectra to N_2^+. But Tanaka (62) showed that all spectra were from NO

or NO^+. The absorption spectrum of NO was studied by Sutcliffe & Walsh (63), who gave interpretations of the electronic states concerned.

In the near ultraviolet and visible regions, a variety of molecules were studied. Rao & Sarma (64) corrected a previous analysis of a transition in CO^+. The spectrum of N_2^+ in the 6890 to 9500 Å region was analyzed by Douglas (65). Porter (66) obtained some bands of ClO in a flash photolysis experiment. CaO and MgO were studied by Patnaik (67) and CaO by Lagerqvist (68), who discussed the electronic transitions involved. Almkvist & Lagerqvist (69) and Kovács & Budó (70) obtained rotational analyses of some SrO bands. Rao (71) made a rotational analysis of some bands of NbO. Barrow & Caunt (72) made a rotational analysis of two bands in the $^2\Sigma^+$-$^2\Pi_i$ system of HBr^+, and Cuthbertson (73) found a new band of He_2. Kleman (74) made a rotational analysis and study of perturbations of some bands of AlH and AlD. AlF was studied by Naudé & Hugo (75) and by Rowlinson & Barrow (76). Barrow & Caunt (77) measured bands in a series of alkali metal fluorides and estimated the heat of dissociation of F_2. K. S. Rao (78) derived theoretical expressions for rotational energy levels of $^5\Sigma$, $^6\Sigma$, and $^7\Sigma$ states and P. T. Rao (79) applied the expressions in an interpretation of the spectra of MnBr and MnF. The spectra of MnH and MnD were studied by Nevin & Stephens (80). Robin & Robin (81) measured absorption coefficients of oxygen in the visible region, at high pressures, and tentatively assigned the spectra to $(O_2)_2$. The absorption of solid NO at 20°K. with maximum near 2100 Å is due probably to N_2O_2 (82).

Simple polyatomic molecules.—Included here are molecules which contain less than ten atoms, together with a few simple polyatomic ions. It is possible, naturally, to arrive at a more complete understanding of the electronic levels of some of these molecules than in the more complicated cases in following sections. Some progress has been made in interpretation of the near ultraviolet formaldehyde spectrum by Dyne (83), who made a rotational analysis of part of the α-band of this system. Dyne also rephotographed the fluorescence spectrum and gave a tentative interpretation of the relations between the absorption and fluorescence spectra. Walsh (8, 84) has discussed this spectrum also in detail, but the interpretations are not to be regarded as final, and more data evidently are required. The vibrational spectrum of Cl_2CS has been studied with high resolution by Duchesne (85). A detailed analysis and treatment of the excited state vibrations showed interaction between C=S and C—Cl vibrations, which indicated some delocalization of the π-electrons of this molecule.

Ingold & King (25 to 28) made a thorough experimental and theoretical study of the lowest electronic transition in C_2H_2. They find that the molecule is bent to a *trans*-form in the upper electronic state, corresponding to sp^2 hybridization of the carbon orbitals. Ramasastry (86, 87) concluded that CS_2 was bent in its lowest excited state, from analysis of the near ultraviolet spectrum. Unpublished work (88) indicates that a similar situation exists in HCN.

The problem of intensities of electronic transitions of simple molecules involves quantitative measurement of integrated absorption coefficients, frequently in the vacuum ultraviolet region. The older methods of photographic photometry have been applied by Moe & Duncan (89, 90) to C_2H_2 and to CH_4 down to about 1000 Å. Measurements on H_2O in the region 1600 to 1750 Å by Johannin-Gilles (91, 92) showed that Beer's law was not obeyed for this transition. Characteristics of photographic plates for this region were studied by Lee & Weissler (93). Other intensity measurements were made by photoelectric methods (94, 95). Watanabe, Inn & Zelikoff (96) reported preliminary measurements on O_2 and on CO_2 by this method, followed by a series of papers reporting measurements down to 1050 Å on ethylene (97), H_2O (98), CO_2 (99), O_3 (100, 101), and N_2O (102). In connection with some of these studies at very short wavelengths, continuous absorption corresponding to ionization is found. Inn (103) developed a method for measuring the threshold for photoionization corresponding to the first ionization potential. The method is more precise than electron impact, and is applicable to cases where spectroscopic methods fail. Wainfan, Walker & Weissler (104) have developed a similar method, and have applied it to photoionization in O_2 and N_2.

All of the foregoing intensity measurements in the vacuum region were made with vapors. Measurement in solution is prevented by solvent absorption in this region for most cases. Potts (105, 106) has discussed purification of solvents and methods of measurement in solid solution at low temperatures down to 1670 Å. The spectrum of pure solid N_2O down to 1600 Å was studied by Romand & Granier-Mayence (107), who observed one band with a maximum at 1780 Å. Hellwege & Hellwege (108) studied the lattice vibrations at high dispersion of crystals of Pr and Nd salts at 14°K. The absorption of sulfur vapor and solution showed the presence of S_8 rings at low temperatures (109). Katzin & Gebert (110) compared the reflection spectra of complex Co salts with their solution spectra and with crystal structure, wherever possible.

Several studies have been made with simple ions in solutions, where interaction with the solvent is shown by the appearance of new bands. For example, Friedman (111) found the positions and separations of the electronic levels of NO_2^-, ClO_2^-, and ClO^- could be correlated with spectra of isoelectronic molecules, but intense bands appearing in solution at shorter wave lengths were ascribed to electron transfer to the solvent. Katzin (112) studied the effect of Ni^{++} and Co^{++} on the absorption of SCN^-, Cl^-, and Br^- ions. Konopic *et al.* (113) found an absorption band characteristic of the ClO_2^- ion in water at 2600 Å .Katzin (114) discussed I_3^- absorption in oxygenated solvents, and solvent interaction with I^-.

Free radical spectra.—Positive identification of spectra of the NH_2 radical has been accomplished by Herzberg & Ramsay (115). Their first observations were made in a flash photolysis apparatus, similar to one described by Porter (116), with ammonia at low pressures. Lines appeared in absorption which

coincided exactly with lines in the "α-band" emitted in NH_3-O_2 flames. The same absorption bands were obtained by Ramsey (117) in continuously irradiated ammonia and in the flash photolysis of hydrazine (118). Herzberg & Ramsey (119) showed that neither NH or NH_3 could be responsible for the spectra and other possibilities (N_2H, N_2H_2, N_2H_3) were eliminated as inconsistent with the observed rotational structure of the bands, and with the isotope effect with photolyzed $N^{15}H_3$ and ND_3.

The flash technique was used by Ramsey (120) to obtain the absorption spectrum of HCO. Rotational analysis showed that the molecule is nonlinear in its ground state, but linear in the excited electronic state. This technique was used also to obtain high dispersion absorption spectra of SH and SD (121). The high frequency discharge, operated under favorable conditions, is a good source for free radical spectra. With a source of this nature Dyne & Ramsey (122) obtained the spectrum of CS, and Dyne (123, 124) observed the spectrum of NH_2 and a new band system from acetylene, due to this molecule or to some radical derived from it. A spectrum probably due to C_2H (or possibly C_2H_2 or C_2H_3) was obtained by Schüller (125) in a high frequency discharge in He containing a trace of an aromatic hydrocarbon. The spectrum also appears with C_2H_2 in the discharge and (with an isotope shift) with C_2D_2. Goupil (126) calculated the separation of the normal and first excited electronic level of a linear C_3 molecule, and found that the interval corresponded to about 4070 Å, which may lend support to the tentative assignment by Douglas (127) to bands in this region found in the spectra of comets and in discharges between carbon electrodes.

The high frequency discharge method for production of spectra of polyatomic radicals or even stable polyatomic molecules has many obvious advantages, but the best conditions of operation are not well understood. It is evident that under some conditions only diatomic spectra are produced. Vacher & Lortie (128) have studied this phase of the problem. A review on technical aspects of operation has been published by Morgan (129).

Benzene derivatives.—Evidence for a new electronic transition in benzene itself has been reported by Ham (130). This overlaps the more intense 2600 Å transition, but it is intensified in a hydrocarbon glass containing CCl_4 at low temperatures. The upper state is thought to be $^3B_{2u}$. But the possibility of assignment of the new spectrum to a molecular complex is not excluded. A new band in the spectrum of benzonitrile (131) was ascribed to a singlet-triplet transition.

Vibrational analyses of a number of absorption and fluorescence spectra of directly substituted benzenes were reported (132 to 137). In all cases the spectra lie near the forbidden transition in benzene at 2600 Å, and the vibrational patterns resemble the familiar pattern shown by benzene, with modifications in detail introduced by the lower symmetry and the presence, in some cases, of vibrations of substituent groups. Garg (138) found in addition to absorption in this region, two other regions in benzaldehyde at longer wave lengths. An emission spectrum attributed to aniline was obtained

by Asundi & Bhattacharya (139) in the high frequency discharge. Schüler & Reinebeck (140) have summarized recent work on high frequency discharge spectra of chlorobenzene.

The effect of hydrogen bonding on the spectra of phenol (141) and phenol, aniline (142) were studied. Bayliss & Hulme (143) discussed solvent effects on intensity of the spectra of benzene and its simple derivatives. Deb (144) compared spectra of ethyl and isopropyl benzenes in liquid and solid states. Burawoy & Chamberlain (145) studied the effect of steric hindrance on inhibition of conjugation, reflected in reduction of absorption coefficients and displacements of electronic levels in substituted phenols.

Other organic compounds.—The smaller molecules, all of which absorb principally in the vacuum ultraviolet region, may be discussed first. The spectrum of cyclopropane in this region was studied by Wagner & Duncan (146), who found four resolved electronic transitions and continuous absorption below 1100 Å. The longest wave length transition showed some vibrational structure, which was given a tentative interpretation. The spectra and absorption coefficients of ammonia and some simple alkyl amines have been studied down to about 1600 Å by Harrison *et al.* (147). Alkyl substitution produces considerable shifts toward the red relative to ammonia, and an increase in intensity of the electronic transitions. Some analysis of the vibrational structure was made, wherever it was resolved. Pickett *et al.* (148) investigated piperidine, pyrrolidine, piperazine, pyridine, and pyrrole in the vacuum region, and compared the effects of cyclization, solvent, size of ring, and number of nitrogen atoms. Simpson (149) studied formamide and dimethyl formamide in the vacuum region. A Rydberg series was found in formamide, leading to an ionization potential of 10.2 ev. An orbital energy diagram was presented and used in interpretation of the electronic transitions. Milazzo (150) studied the emission spectrum of *n*-methyl pyrrole in the high frequency discharge and noted the remarkable stability of the molecule under these conditions.

Several contributions toward the interpretation of the longest wave length transition in naphthalene have been made recently, but the question whether it is forbidden ($g \rightarrow g$) or allowed ($g \rightarrow u$) is not settled. Internal evidence from analysis of the fluorescence spectrum (151), absorption in polarized light (152), and temperature dependence of intensity of absorption (153) point to a forbidden $A_g \rightarrow A_g$ transition. Evidence for an allowed transition comes principally from intensity and direction of dipole moment in substituted naphthalenes (154), interpreted in connection with Platt's theory (155) of parity. Craig & Hobbins (156) studied anthracene crystals with polarized light and concluded that there were two transitions with different polarizations in the 3800 Å region. Fluorescence spectra of anthracene, phenanthrene, and chrysine were studied at temperatures down to 14°K. over a wide range of pressures (157). Wenzel (158) concluded from a study of spectra of substituted diphenyls that there were two transitions in diphenyl in the 2500 Å region.

Acetophenone and benzophenone were studied by Imanishi *et al.* (159). They found two regions of absorption: one characteristic of the C_6H_5 group showed elaborate vibrational structure, but the other region, characteristic of the C=O group, showed only continuous absorption. A similar result with acetophenone was obtained by Viswanath (160) and by Vanselow & Duncan (161). The latter obtained a blue fluorescence spectrum from the solid and from a solid solution, similar to fluorescence spectra of other ketones.

Two electronic transitions in α-, β-, γ-picolines were studied by Rush & Sponer (162) and the vibrational patterns were analysed. The longest wave transition was attributed to excitation from a nonbonding orbital of nitrogen to a π-ring orbital; the higher energy transition was attributed to π-electron excitation. Lyons (163) used polarized ultraviolet light in the assignment of electronic transitions in some pyrimidines. The spectra of some tautomeric pyrimidines were studied by Boarland & McOrmie (164). Kaibu (165) studied hydrogen bonding in pyridine with various solvents.

Steric effects of NO_2 and NX_2 (X is halogen) groups on inhibition of conjugation in spectra of aromatic sulfides and sulfones were found to be large (166). Substitution in methyl silbene produced changes in position and intensities of the lowest electronic transitions, attributed by Beale & Roe (167) to steric hindrance. Their theoretical results were discussed by Platt (168) who offered additional suggestions in regard to interpretation. Brode *et al.* (169, 170) continued their investigation of *cis-trans* isomerism in aromatic azo dyes, and obtained separate absorption curves for the short-lived *cis* isomer.

With the growing importance of polymers, spectra of these materials is of interest. Klevens (171) compared the spectra of polymers and monomers containing the same chromophoric groups, and found little change in the positions of absorption bands. Also it appears that the spectra of polystyrene (172) are identical with ethylbenzene, and that the principal absorption is localized in the benzene ring to such an extent that the vibrational structure characteristic of benzene derivatives is present.

Molecular complexes.—Many investigations which were discussed previously in this review were concerned with the effect of solvent on positions and intensities of electronic transitions, but in most cases the interactions were mild, so that spectral shifts rather than new spectra were evident. [See, however, (111, 112, 114).] With stronger interactions, new spectra of molecular compounds or complexes of varying stability appear, which are not present in the parent molecules. While this has been known for a long time, interest has been stimulated recently by quantum mechanical theories of Mulliken (173, 174) and correlations of such spectra by McConnell, Ham & Platt (175). Space allows mention of only two other papers on this interesting subject. Lawrey & McConnell (176) have studied the spectra of a 1:1 complex of benzene and *s*-trinitrobenzene, which showed four electronic transitions (not present in either single molecule) in the 2100 to 4100 Å region. A number of absorption bands have been found (177) in solutions

of I_2 in saturated hydrocarbon-alkyl halide solvents which are not present in either I_2 or solvent alone. A perturbation theory was developed which was successful in prediction of the positions of the principal transitions.

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THE SOLID STATE[1]

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Solid-state research has accelerated and burgeoned so enormously in the immediate past that a complete annual review would be unduly long. We concentrated, instead, on the general status in a few representative areas, especially in synthesis, theory, and trapping and magnetic phenomena.

Synthesis and Structure of Solids (H. W. Leverenz)

From the chemical standpoint, the preparation of solids continues to be an art. Even the gross atomic arrangements of new solids are rarely predictable. Similarly, the space groups of many long-known solids, such as $CdSiO_3$ and β-Zn_2SiO_4 (quenched from a melt), are still unknown. On a finer scale of atomic arrangement, more detailed knowledge of the electronic structures of atoms and ions would be required to predict that $Mn^{(2+)}$ substitutes for 4-coordinated $Zn^{(2+)}$ in rbhdl.-Zn_2SiO_4, but substitutes for 6-coordinated $Fe^{(2+)}$, instead of 4-coordinated $Zn^{(2+)}$, in cub.-$ZnFe_2O_4$ [Jenkins, McKeag & Rooksby (1); Verwey & Heilmann (2)]. There are variable proportions of heteropolar and homopolar bonding that influence this behavior, and it is because there is uncertainty about these proportions that the ionic superscripts are put in parentheses. In spinels, Romeijn (3) has shown that the distribution of ions in available lattice sites is governed by the electronic distributions in the ions, as well as by the co-related sizes of the ions. More knowledge of the electronic structures of atoms is required also to calculate their polarizabilities and explain the enormous mobilities of charge carriers in semiconductor compounds, such as the cub.-InSb reported by Welker (4).

On a still finer scale, there is much to be done about the unavoidable, and deliberately produced, imperfections that profoundly influence many properties of solids [Leverenz (5); Stöckmann (6)]. The kinds, proportions, and distributions of the chemical and physical imperfections in solids depend strongly on the details of their preparation. This important feature of solids was treated in a Symposium on Impurity Phenomena (7), including papers by Seitz, by Wagner, by Pound, by Schulman, and others.

The purest germanium, perhaps our most refined substance, contains at least 10^{12} impurities per cm.[3] [Shockley (8)]. That is a very small proportion of chemical imperfections relative to the 10^{22} germanium host-crystal atoms; nonetheless, the residual impurity atoms affect both the minority charge-carrier lifetime and the low-temperature conductivity of germanium crystals. It is probable that the proportions of physical imperfections such as omission

[1] The survey of the literature pertaining to this review was completed in December, 1953.

defects, displaced atoms, and dislocations, are often higher than the proportion of impurities [Seitz (9); Mott (10)]. Uncontrolled variations in the preparations of solids, especially electronically active solids, frequently produce marked and unexpected variations in their properties.

Zinc oxide, for example, is notorious for variability in natural color, luminescence, and electrical conductivity. Thomsen (11) showed that sulfur in trace amounts, rather than a presumed excess of zinc, functions as the main luminescence activator. Pronounced changes in color, structure, and conductivity are produced by changes in atmosphere during high-temperature heating [Kutzelnigg (12); Archard (13); Scharowsky (14)]. Conductivity, in particular, can be changed by several orders of magnitude when zinc oxide is heated in an atmosphere of one or the other of its constituents. At present, all these differently behaving materials are designated as zinc oxide, or ZnO, which implies that they are identical. One of the goals of physical chemistry, as applied to solids, is to evolve means for distinguishing and denoting ostensibly similar materials having different physical characteristics.

From the physical standpoint, the fundamental laws for the interactions of the elementary particles of which solids are composed are believed known. Some of the laws, such as the electrostatic interaction of two charged particles, are simple and known exactly. Others, such as exchange interactions and correlation effects, are complex and known approximately. As Rice & Teller (15) have pointed out, the properties of only the very simplest lone atoms can be calculated more economically than they can be determined experimentally. Calculations of the properties of more complex atoms, and assemblages of atoms, are so approximate and time-consuming that the experimental approach is still the most fruitful for general use in the solid-state field. Some of the properties of ideal simple solids, however, can be calculated with the energy-band theory previously outlined by Smoluchowski & Koehler (16), and Williams (17). Solid-state theory has had heuristic value, and has provided the well-known energy level and configurational-coordinate diagrams that are invaluable as orderly frameworks by means of which descriptions can be made of many of the physical properties of solids.

Quantum Theory of Solids (Frank Herman)

During the past few years many important theoretical developments have taken place in solid-state physics. In general, the energy band scheme has proved quite successful. Most physical processes occurring in crystals have been correlated with the electronic structures of these crystals. However, it is becoming increasingly clear that many observations will not be satisfactorily explained until more refined and more sophisticated models are available.

A reasonably complete understanding of superconductivity, to cite one example, will undoubtedly be achieved only after the underlying physical mechanisms are discovered and thoroughly examined, and suitable mathematical techniques evolved to describe these mechanisms. On the other hand,

a convincing interpretation of many crystal phenomena which today seem puzzling should require little more than a deduction of the consequences of a particular type of energy band structure. Unfortunately, it is no simple task to determine the electronic structure of a real crystal.

General survey.—Many significant contributions to the formal theory of electrons in perfect and in nearly-perfect crystals have been made in recent years. The Wannier function formalism has received particular attention. Several methods of approximation have been proposed for solving the Schrödinger equation for a perfect periodic potential and for a perturbed periodic potential. The energy band structures of many actual crystals have been calculated on the basis of the usual simplifying assumptions. Large-scale automatic computing machinery now plays an important role in such investigations.

Since many electrical and optical properties of crystals depend in no small measure upon the nature of the imperfections present, the eigenstates of electrons at spatial inhomogeneities have been intensively studied. Progress has been made in treating the absorption of light by trapped electrons, the thermal ionization of trapped electrons, and the screening of ionized impurity atoms by free carriers.

There have been many theoretical advances in the description of free electrons in crystals in the presence of a magnetic field. Spin paramagnetic resonance and diamagnetic resonance measurements conducted at microwave frequencies have already provided valuable information on both free and bound electronic states.

Many refinements in the theory of electron mobility in crystals have been achieved as a result of investigations of the interaction between electrons and (*a*) lattice vibrations, (*b*) ionized impurity atoms, (*c*) neutral impurity atoms, (*d*) vacancies, (*e*) dislocations, and (*f*) high electric fields.

When the mean free path of an electron becomes comparable to or larger than the characteristic dimensions of the crystal, complicated effects occur. At high frequencies, when the period of the impressed electric field becomes equal to or less than the time between electron-atom collisions, additional effects can take place. Such situations have been thoroughly examined and, as a consequence, our understanding of the anomalous skin effect (mean free path larger than classical skin depth) and of the conductivity of wires and thin films is much improved.

The theory of the motion of slow electrons in ionic crystals has been put on a firmer theoretical foundation. Since the effective mass of a polaron (slow electron plus associated ionic polarization) is found to be only slightly larger than the free electron mass, self-trapping now appears to be a highly unlikely process.

One of the most fundamental problems in solid-state physics is the description of electron-electron interactions. In the Hartree-Fock scheme, each electron is treated as moving in the time-averaged field of all the other electrons. This approach leaves much to be desired. In the past few

years, a collective description of electronic interactions has been developed and many interesting consequences of this work have already been derived.

Probably the most important theoretical advance in solid-state physics in recent years is the recognition by Fröhlich (18), and independently by Bardeen (19), that the interaction between electrons and lattice vibrations is intimately related to the occurrence of superconductivity. This may well be the key to the understanding of this effect. It is conceivable, however, that superconductivity will be satisfactorily explained only by a theory which takes cooperative effects into account more fully than the band scheme does.

Among the more extensively investigated crystals during the last few years are silicon and germanium. Yet many of the effects observed in these crystals are not completely understood. For example, why does *p*-type germanium exhibit two distinct diamagetic resonances, as the experiments of Dresselhaus, Kip & Kittel (20) reveal? It is likely that such phenomena will seem much less mysterious than they do today as soon as the energy band structures of these crystals are known in sufficient detail.

Shockley (21) has already offered an ingenious interpretation of the anisotropic magnetoresistance observed in germanium in terms of a complicated energy band scheme. Briggs & Fletcher (22) have presented an explanation of the infrared absorption in germanium associated with free holes which is also based upon an intricate band structure.

More accurate knowledge of the energy band structure of crystals should eliminate the undesirable role the "effective mass" now plays as the much-needed adjustable parameter in a variey of theoretical relationships.

Kittel (23) has written a very readable introduction to solid-state physics. The second edition of Wilson (24) contains a comprehensive and up-to-date treatment of mobility theory and of various magnetoresistive, thermomagnetic, and thermoelectric effects. As the title of Wilson's book states, the emphasis is on metals; however, semiconductors and insulators are discussed briefly. About the best treatment now available of semiconductor physics is that given by Shockley (25).

Because of space limitations, the present survey will not attempt to cover any of the interesting developments that have taken place in recent years in the fields of low temperature physics, ferromagnetism, radiation damage, crystal growth, and dislocation theory. The interested reader is referred to the following textbooks and review articles for further information on the following subjects: low temperature physics—London (26), Shoenberg (27), and Squire (28); ferromagnetism—Slater (29) and Wohlfarth (30); radiation damage—Slater (31) and Dienes (32); crystal growth and dislocation theory—Nabarro (33), Cottrell (34), Read (35), and Verma (36).

Energy band theory.—Slater (37) has written a very useful introduction to the energy band theory. In this, many of the well-known approximate methods for solving the wave equations for a perfect crystal are described and compared. It is also shown how symmetry considerations can be exploited to simplify the formulation of the crystal eigenvalue problem.

In order to elucidate the nature of Wannier functions, the degeneracy of energy bands, and the influence of perturbations on crystal eigenfunctions, Slater (38) has investigated the energy band structure of idealized one-, two-, and three-dimensional crystals.

Slater (39) and Saffren & Slater (40) have recently proposed a new method of approximation which they call the "augmented plane-wave method."

Much attention has been devoted during the past few years to Wannier's theorem relating to the motion of an electron in a perturbed periodic potential and to Wannier functions. The Wannier function formalism offers a powerful approach to the further development of many aspects of energy band theory.

Adams has made several important contributions to the formal theory of Wannier functions. He has generalized and extended (41) the earlier derivation by Slater (42) of Wannier's theorem. Adams (43) has presented an elegant treatment of an electron in a magnetic field with the aid of his generalized "multi-band" Wannier formalism. He has also derived anew (44) the "effective mass" equation.

Kohn (45), Koster (46), and Parzen (47) have formulated the crystal eigenvalue problem as an application of the variational principle, Koster and Parzen making use of Wannier functions in their work. Kohn's paper serves to clarify the underlying basis of various schemes of approximation. Kohn arrives at an interesting interpretation of the cellular method by adopting the viewpoint of the variational principle. Koster (46) describes how group theory can be used to simplify the construction of Wannier functions.

Feuer (48) shows how large over-all perturbations can be treated by Wannier function methods. She investigates the Zener effect in an idealized crystal. For a typical experimental situation her results predict onset of Zener breakdown at a smaller electric field than that given by Zener's original formula. However, it must be borne in mind that Zener's work (49) was also based on an idealized crystal model.

Raynor (50) has recently published a comprehensive review of the development of the electron theory of metals. He shows how many of the physical properties of metals can be correlated with the calculated energy band structures. In general, the monovalent metals give less trouble than the multivalent metals. Raynor discusses the nature of the transitional metals and considers how band theory can be applied to alloys.

The band structures of the following crystals have been investigated during the past few years: sodium—Howarth[2] & Jones (51); silicon—Holmes (52); barium oxide—Morita & Horie (53); beryllium—Donovan (54); lead sulphide—Bell and co-workers (55). Each of these calculations was performed by means of the Wigner-Seitz-Slater cellular method. It is regrettable

[2] Using the same approach, Howarth has recently studied the copper crystal (51a).

that considerations of space permit no more than a mere mention of these papers.

The band structures of the following crystals have recently been studied by the method of orthogonalized plane waves originally introduced by Herring (56): lithium—Parmenter (57); diamond—Herman (58); germanium—Herman & Callaway (59).

In both diamond (58) and germanium (59), the conduction band states of lowest energy at the central point of the reduced zone were triply-degenerate, rather than nondegenerate as earlier studies of diamond and silicon had suggested. The occurrence of spherical energy surfaces for electrons in diamond and germanium (and probably silicon as well) is ruled out, therefore, by symmetry considerations. Nonspherical and/or degenerate energy bands had been anticipated by Shockley (21) on the basis of his interpretation of the anisotropic nature of the magnetoresistance observed in germanium by Pearson & Suhl (60).

Much theoretical work remains to be done on the band structure of germanium before certain experimental results, such as the cyclotron resonances observed by Dresselhaus, Kip & Kittel (20) can be understood. Adams (61) has commented recently on the theoretical situation as it appears at present.

Fletcher (62) has investigated the structure of the *3d* bands in nickel and has deduced the density of states and the total width of these bands. The possible existence of electronic bound states at the surface of a metal has been studied by Baldock (63). Both Fletcher (62) and Baldock (63) use the tight-binding approximation, which we will abbreviate as TBA.

Hall (64) has determined the valence band structure of the diamond crystal by the "equivalent orbital" method. This approach leads to the same type of secular determinant as the TBA but the point of view is different in that Hall evaluates the matrix elements with the aid of empirical data. Slater (65) has proposed a new method for determining energy band structures in which the TBA is employed as an "interpolation scheme." In this manner, Slater & Koster (66) have studied the diamond crystal using the results of Herman's work (58) as the starting point.

Impurity states.—The energy of electrons trapped at an impurity carrying an extra positive charge in ionic crystals has been investigated by Lehovec (67). He derives the thermal and optical activation energies corresponding to electronic transitions from the lowest bound state to the conduction band on the basis of a simplified model.

At sufficiently high impurity concentrations, trapped electrons can interact with each other giving rise to "impurity bands." The electrical conduction that can occur through the agency of impurity bands has been studied by Baltensperger (68) and by Aigrain & Jancovici (69). On the assumption that the usual band theory can be applied, Baltensperger determines the extent to which impurity band conduction occurs as a function of impurity concentration and temperature. A random distribution of impurity centers is the essential feature of the model employed by Aigrain and Janco-

vici. They find that the density of levels at the bottom of the impurity band increases as the square root of the energy, as in the usual band theory, but, due to the assumed random distribution, there is an infinite exponential tail toward high energies. They use this result to interpret various low temperature data.

Erginsoy (70) has studied the structure of impurity bands on the basis of the cellular approximation. He finds that with increasing impurity concentration, a continuous decrease in the activation energy from its hydrogenic value to zero cannot be accounted for by interactions among trapped electrons alone.

James & Ginzbarg (71) have investigated the band structure of a one-dimensional model of a disordered alloy. Their analysis also applies to the case of a crystal with randomly placed impurities. The random aspect of the problem is fully taken into account and the assumption is not made that the deviation from periodicity is small. An illustrative calculation on a linear model shows how the sharply defined "impurity band" of a crystal with regularly placed impurities is replaced by a broadened region when the impurities are randomly arranged.

The statistics of the recombination of holes and electrons in semiconductors has been analyzed by Shockley & Reed (72). Their model requires recombination to occur through the mechanism of trapping.

Optical phenomena and lattice vibrations.—Briggs & Fletcher (22) have measured the infrared absorption associated with free carriers by injecting electrons and holes into germanium. They find that the absorption by the minority carriers in *n*-type germanium is peaked at the same wavelengths, i.e., at 3.4 and 4.7 microns, as the absorption by majority carriers in *p*-type germanium. Briggs and Fletcher attribute the absorption maxima to inter-valence-band electronic transitions. The key assumption of this theory is that the highest energy states for holes do not occur at the central point of the reduced zone, since here the three valence bands involved are degenerate (59). Further developments in the band theory of germanium are required to verify the correctness of this interpretation.

The nature of the analytic singularities to be expected in the frequency distribution of the lattice vibrations in one-, two-, and three-dimensional crystals has been elucidated in an important paper by van Hove (73). The distribution function for a two-dimensional crystal has logarithmically infinite peaks. In the three-dimensional case, the distribution function itself is continuous but its first derivative exhibits infinite discontinuities. These results are a consequence of the periodic structure and are derived on the assumption of harmonic interatomic forces.

Simeral (74) has interpreted the infrared absorption associated with lattice vibrations in diamond, silicon, and germanium as follows. The selection rules normally forbidding fundamental absorption are broken down in diamond because of the presence of impurities, and in silicon and germanium because of the presence of more than one isotope. He correlates many of the

observed absorption maxima with one-phonon or two-phonon processes. In diamond, some of the absorption in the fundamental band cannot be related to lattice vibration excitation.

De Launay (75) has modified the Born-von Karman lattice dynamics to include the role played by the conduction electrons in acoustical wave motion. De Launay finds that the well-known discrepancy in the Cauchy relation for various crystals can be related to the bulk modulus of the electron gas.

Krumhansl & Brooks (76) have evaluated the frequency spectrum of the lattice vibrations of graphite and have shown that the variation of specific heat according to the square of the temperature (instead of the usual variation with the cube of the temperature), observed between 15° and 80°K., is a consequence of the elastic anisotropy of graphite. The graphite frequency spectrum has also been determined by Rosenstock (77).

The theory of the anomalous skin effect in metals has been extended by Holstein (78), Dingle (79), and Chambers (80). According to Dingle, the theoretical optical properties of metals can be brought into better agreement with the observed behavior if the anomalous nature of the skin effect is taken into account and if the reflection of electrons at the metallic surface is assumed to be diffuse.

Butcher (81) has studied the absorption of light arising from interband electronic transitions in alkali metals. His model leads to an absorbing power which can be fitted reasonably well to the experimental data for sodium, potassium, and rubidium. Butcher's treatment does not appear adequate, however, in the case of cesium.

The rate of thermal ionization of a trapped electron determined by Kubo (82) is, in general, greater than that obtained earlier by Goodman, Lawson, & Schiff (83). A clarification of this process, and hence its complementary process, the radiationless transition of an electron from the conduction band to an impurity state, would be most desirable.

The validity of the Franck-Condon principle as applied to crystals has been investigated by Lax (84). Lax calculates and compares the total absorption, the mean absorption frequency, and the breadth of the absorption line predicted by various forms of the Franck-Condon principle.

Both Lax (84) and O'Rourke (85) have shown how to treat the absorption of light by trapped electrons and how the results obtained earlier by Huang & Rhys (86) can be derived more simply.

Dexter & Heller (87) have computed the polarizability of an atom in an idealized insulating crystal. They relate the polarizability given by the Lorentz local field method to the dipole-dipole interactions. Corrections to the Lorentz value are found to arise from exchange and overlap effects and from multipole interactions other than dipole-dipole.

Huang (88) has clarified the nature of the interaction between a radiation field and an ionic crystal. Huang (89) has also developed an atomic theory of elasticity and a theory of dielectric and piezoelectric constants of crystals.

His work represents an important contribution to the theory of ionic crystals.

The temperature dependence of the threshold frequency for optical absorption in insulating cyrstals has been investigated by Cheeseman (90). He assumes that the long wave absorption edge is determined by second order processes. i.e., by transitions in which an electron absorbs a photon and simultaneously emits or absorbs a phonon. The theoretical temperature shift calculated by Cheeseman is linear in temperature and, in the case of cadmium sulphide, is found to be of the same order of magnitude but somewhat smaller than that observed experimentally.

Diamagnetism.—The diamagnetism of electrons in crystals has been investigated theoretically by various authors, including Sondheimer & Wilson (91), Dingle (92), Wilson (93), Band (94), Ham (95), Osborne (96), Steele (97), and Adams (43).

Electron mobility in metals.—The theory of electron mobility in metals has been improved considerably during recent years. There has been much work on electrical and thermal conductivity, expecially at low temperatures.

Klemens (98), in an important paper, has demonstrated that equilibrium between electrons and phonons at low temperatures can be established by the anharmonic lattice forces alone and that Umklapp processes are not required to maintain the steady state.

Chambers (99) has presented a kinetic formulation of conduction problems. This simplified treatment is based on an integrated form of the Boltzmann transport equation and has already shown its usefulness in an earlier study by Chambers (100) of the conductivity of a thin wire in a magnetic field.

Rhodes (101) has solved the Bloch integral equation for the electrical conductivity over a much wider temperature range than had previously been attempted. Rhodes' work makes it possible to compare the predictions of electron mobility theory with experimental data not only at low and high temperatures, but at intermediate temperatures as well.

Sondheimer (102) has reviewed the theory of the mean free path of electrons in metals. He is particularly interested in cases in which the mean free path can be obtained directly by measuring the conductivity under conditions where the free path may be compared with some other characteristic length in the metal. The anomalous skin effect of metals and the conductivity of thin films and wires fall within the purview of Sondheimer's discussion.

MacDonald & Sarginson (103) have reviewed galvanomagnetic effects in conductors, particularly in metals.

Dexter (104) has investigated the role of scattering by point singularities in establishing the electrical resistance of metals. This problem is of interest in radiation damage studies, since one method of estimating the extent of radiation damage involves measuring the change of resistance with irradiation. Dexter finds that the contribution to the electrical resistance arising from lattice distortions associated with vacancies, interstitials, and substitu-

tional atoms is negligibly small for the imperfection concentrations normally encountered.

A comprehensive theory of the change in the electrical and thermal properties of monovalent metals produced by lattice distortions has been developed by Sáenz (105).

Several authors, including Mackenzie & Sondheimer (106), Landauer (107), and Dexter (108, 109) have developed formulas for the resistivity due to scattering of electrons by edge dislocations. Dexter (109) shows that the resistivity is anisotropic, the slip direction being the direction of low resistivity.

Parmenter (110) has predicted that a sound wave traveling in a solid can generate an electric current. Parmenter also discusses the conditions under which this "acoustoelectric" effect could be observed.

Electron mobility in polar semiconductors.—Electrical conduction processes in polar semiconductors have been investigated in an important paper by Howarth & Sondheimer (111). They are concerned primarily with cases in which electron scattering by the optical modes is the dominant electron-lattice interaction. They find that at low temperatures a unique relaxation time cannot be defined. The mobility at low temperatures is carefully analyzed. The universal relaxation time that can be defined at high temperatures is identical with the value derived earlier by Fröhlich.

The scattering of electrons by acoustical modes in polar crystals has been studied by Meijer & Polder (112). In the case of zinc sulfide (sphalerite), it is found that the acoustical modes, which are here piezoelectrically active, become as important as the optical modes at 150°K. and below. It is also demonstrated that the acoustical modes in crystals having the sodium chloride structure can scatter electrons as effectively as the optical modes, provided the mass difference of the positive and negative ions is sufficiently great. The relaxation times for the two types of scattering become equal at about 200°K. in the case of lithium fluoride.

Electron mobility in nonpolar semiconductors.—Shockley (113) has offered an interpretation of the electric field dependence of the electron mobility observed in *n*-type germanium. At low fields, where ordinary mobility theory applies and Ohm's law is obeyed, the drift velocity varies linearly with the field. Here, the predominant interaction is between electrons and the acoustical phonons. At intermediate field strengths, unlike the low field case, the electrons are unable to dissipate the energy they acquire from the field by collisions. In consequence, the electron "temperature" is raised and the drift velocity varies as the square root of the field strength. Shockley suggests that, at sufficiently high fields, the strong interaction between electrons and the optical phonons leads to a limiting electron drift velocity.

Conwell (114) has explained the different variation of electron mobility with electric field observed in the same *n*-type germanium sample in different temperature ranges as follows. At very low temperatures (20°K.), the scattering by ionized impurities is more important than lattice scattering

for electron temperatures of the order of the lattice temperature. This leads to a steep initial increase in the mobility versus field intensity curve. After a small range of fields, this increase results in the impurity scattering becoming less effective than lattice scattering, and the square root of field variation characteristic of this mechanism sets in.

Bardeen & Shockley (115) have critically examined the scattering of electrons in the presence of large electric fields. They conclude that the probabilities of scattering by lattice vibrations or imperfections are independent of electric field intensity up to fields of the order of 6×10^5 volts/cm. Conwell (116) has derived a relationship between mobility and relaxation time valid over a wide range of electric fields. At high fields, Conwell's formula yields a field-dependent mobility.

A formula for the resistivity arising from neutral impurity scattering in semiconductors has been derived by Erginsoy (117). Brooks (118) and Herring (119) have refined the Conwell-Weisskopf formula for ionized impurity scattering by taking into account the screening of the ionized impurities by the free carriers present.

Dexter & Seitz (120) have derived a formula for the resistivity arising from dislocation scattering in semiconductors. They find that the reciprocal of the mobility varies as the reciprocal temperature. Dexter and Seitz discuss the relative magnitudes of the terms associated with scattering by lattice vibrations, impurity atoms, and dislocations.

The differential equations governing the flow of electrons and holes in semiconductors under a variety of experimental conditions have been analyzed by Van Roosbroeck (121), Prim (122), Shockley & Prim (123), Dacey (124), Brown (125), and Moss *et al.* (126). These investigations have clarified the behavior of various semiconductor devices. Unfortunately, space considerations preclude more than just a mention of these papers.

Polarons.—Interesting mathematical problems arise in the treatment of slow electrons in ionic crystals because the electron is strongly coupled to the lattice by virtue of the ionic polarization which it induces. The effective mass of the polaron can be calculated with reasonable rigor only by methods which are valid for this situation. Lee, Low, & Pines (127), Gurari (128), and Lee & Pines (129) have investigated the problem and have obtained results for the polaron effective mass which approach the earlier result of Fröhlich, Pelzer, and Zienau in the limit of weak coupling. The new results are valid for a wider range of coupling strength than the earlier ones.

Plasma oscillations.—Bohm & Pines (130–133), in an important series of papers, have developed a collective description of electron interactions. They find that an electron gas displays both collective and individual particle aspects. Long-range Coulomb interactions give rise to organized electron motions known as plasma oscillations. The short-range interactions between individual electrons are of the screened Coulomb type.

Pines (133) makes use of the collective description to estimate the correlation energy of a free electron gas. His results are in good agreement

with the earlier work of Wigner (134). Pines (135) has also applied the collective description to a study of the stopping power of a metal for charged particles. The impinging particles are found to lose energy to the conduction electrons by exciting plasma oscillations and by short-range encounters with individual electrons. The stopping-power formula determined by Pines is similar to that obtained earlier by Kramers and Aage Bohr using other methods.

Pines & Bohm (131) regard the Ruthemann-Lang experiments as verifying their prediction that fast electrons passing through thin metallic films can suffer discrete energy losses by exciting plasma oscillations.

Wolff (136) has investigated the effect of a crystal lattice upon plasma oscillations. He has also studied how plasma oscillations are affected by interband electronic transitions. Wolff is able to explain why the transition metals show broader absorption maxima than the alkali metals in the Ruthemann-Lang experiments. Interband electronic transitions in the transition metals produce the broadening.

Van der Ziel (137) has developed a theory of the production of secondary electrons in solids on the basis of the screened Coulomb interaction between electrons predicted by the Bohm-Pines theory (130–133). This theory appears to be more satisfactory than the one proposed earlier by Dekkar & van der Ziel (138) in which an unscreened Coulomb potential is employed. The theory of secondary emission has also been studied recently by Baroody (139) and by Marshall (140).

Traps in Solids (R. H. Bube)

Research in the electronic properties of solids has progressively revealed that in real crystals the forbidden gap is "forbidden" in name only. Not only has it been found that the forbidden gap is occupied by a host of various types of levels, but in most cases the presence of at least a portion of these levels is essential for the desired electronic behavior.

The concentration and type of levels located in the forbidden gap depends on both the chemical constitution (presence of impurities) and the structural condition (presence of crystal defects). In general, levels lying near the allowed bands have been called trapping levels, whereas levels lying near the center of the forbidden gap have been called recombination levels or centers. With suitable variation of the external conditions, any level can act in a number of different ways.

An imperfection formed by the incorporation of silver impurity in zinc sulfide (giving a level 0.55 ev above the filled band) [Bube (141)] may act as a hole trap; the trap is filled by capture of a hole from the filled band, as in the mechanism for energy transfer by hole migration [Klasens (142)]; the trap is emptied by thermal or optical excitation of an electron from the filled band, as in thermal or optical quenching of luminescence. The same silver-impurity imperfection in zinc sulfide can be considered to be a luminescence center, where the recombination of electrons and holes can occur with the emission of a characteristic blue (2.77 ev) emission.

Other examples of electron trapping associated with the presence of chemical impurities are (*a*) when the impurity has a variable valence, as have samarium, tin, and arsenic [Leverenz (143)]; and (*b*) when oxygen is present in the preparation of ZnS phosphors, either to form trapping centers directly or to aid in the formation of crystal defects which may act as trapping centers [Kroeger & Dikhoff (144); Hoogenstraaten (145)].

Trapping levels associated with crystal defects are present in all real crystals. The concentration of these levels usually varies between 10^{12}/cm.^{3} and 10^{18}/cm.^{3}, depending on the purity and preparation conditions of the material.

The importance of crystal defects in the formation of trapping centers has been shown by Bube by a variety of measurements on the luminescence properties of ZnS phosphors (146). It is found that (*a*) traps occur in phosphors without added impurity; (*b*) trap depths are independent of the added impurity but are characteristic of the ZnS host-crystal; (*c*) the number of traps, as determined by glow-curve areas, increases exponentially with the reciprocal preparation temperature; (*d*) intensification effects are found in which an added impurity (a halide, for example) increases the number of host-crystal emission centers and host-crystal trapping centers; and (*e*) the excitation of photoconductivity varies in the same way with excitation energy as the production of trapped electrons, indicating a separate identity for emission centers and trapping centers.

A unified picture of the complex phenomena of photoconductivity has been proposed by Rose (147) on the basis of a model with levels distributed reasonably uniformly over the forbidden gap. The experimental finding with CdS of a photocurrent varying linearly with the light intensity, and a decay time varying inversely with the light intensity, appears to require such a distribution of levels throughout the region of the forbidden gap traversed by the steady-state Fermi-level in such measurements. These levels are to be associated with crystal defects in the photoconductor crystal.

One of the most useful measurements to give information about the distribution of trapping levels is the luminescence glow curve, or its analogue, the curve of thermally stimulated current for a photoconductor [Bube (148)]. This measurement consists of cooling the sample to a low temperature, irradiating the sample to produce trapped electrons, removing the exciting radiation, and then heating at a linear rate while observing the phosphorescence emission or the current. When the thermal energy which a trapped electron may acquire from the crystal is sufficient to free it from the trap, it will be raised to the conduction band, contribute to the current, and then finally be captured at a recombination center with the emission of radiation or with a nonradiative dissipation of energy as phonons. Detailed measurements of both the luminescence emission and current due to such trap emptying on the same crystal provide valuable data for a comparison of the luminescence and photoconductivity processes.

The measurement of the thermally stimulated current is a more powerful method of obtaining information about trapping levels than the luminescence

glow curve in at least two ways. (*a*) Only traps from which freed electrons give radiative transitions at recombination centers can be detected by the luminescence glow curve; any traps from which freed electrons enter the conduction band or contribute to the photoconductivity in any other manner may be detected by the measurement of thermally stimulated current. (*b*) In converting the data of luminescence glow curves to quantitative values, two unknowns are contained in the equation relating trap depth and the temperature at which the maximum glow intensity is observed: the trap depth and the attempt-to-escape frequency for electrons in traps (actually the product of the true frequency and the transition probability from trap to conduction band). Either one of these values must be assumed and the other calculated, or subsidiary experiments must be performed to determine the trap depth and the frequency independently. In the measurement of thermally stimulated current, however, the trap depth can be obtained directly from a calculation of the location of the steady-state Fermi-level from the conductivity and temperature of the maximum current, and then the attempt-to-escape frequency may be obtained independently from the equation relating trap depth and attempt-to-escape frequency. Having a reliable value of the frequency then makes possible the calculation of a reliable capture cross-section for the traps.

Measurements of trap distribution by these methods indicate an approximately continuous distribution of trapping levels with concentrations at particular energies, or at least a superposition of a number of broad levels.

Magnetic Solids (H. W. Leverenz)

Much of the recent work on antiferromagnetism and ferromagnetism in solids is summarized in a symposium volume of some 70 papers (149), including contributions by Néel, by Shull, by Zener, and many others. In ferromagnetic spinels ("ferrites"), there is a primary antiferromagnetic interaction of unequal numbers of transition-group ions in two dissimilar lattice sites that produces ferromagnetic domains containing the aligned unpaired electron spins of the excess ions in one type of site [Néel (150); Bozorth (151)]. These non-remanent cubic-structure ferromagnetic solids have become industrially important, especially for use at high frequencies [Harvey, Hegyi & Leverenz (152); Fairweather, Roberts & Welch (153); Went & Gorter (154); Weisz *et al.* (155)]. Excellent permanent magnets of the oxide type may be made from certain solids having high magnetic anisotropy, notably mixed oxides of iron and cobalt [Guillaud (156)], and from certain proportions of barium and iron oxides [Went *et al.* (157); Wijn (158, 159)]. Rooksby & Willis (160) find that small but definite structural deformations accompany the abrupt magnetic transitions observed when $CoFe_2O_4$ is cooled.

Gorter & Shulkes (161) have demonstrated that the sign of spontaneous magnetization of a lithium-chromium-iron spinel can be reversibly changed by varying the temperature of the material. The effect is caused by a differ-

ence in the thermal energy required to de-align spins of ions in 4-coordinated and 6-coordinated sites. The *g*-factor of the material was shown by van Wieringen (162) to undergo an anomaly at the compensation temperature where there is no net magnetic intensity. Kaplan & Kittel (163) have analyzed selection rules for magnetic-dipole transitions in ferrospinels, and conclude that it is necessary to have different *g*-factors for the 4- and 6-coordinated ions in order to obtain transitions affording direct experimental determination of the exchange interaction between the ions.

Another interesting feature of ferromagnetic spinels is that they can be used as "gyrators" to produce a Faraday-effect rotation of the plane of polarization of radiation at microwave frequencies [Hogan (164)]. Rowen (165) found that the best performance was obtained from the composition $Ni_{0.3}Zn_{0.7}Fe_2O_4$ when there was about one percent less iron than the formula requires. A type of gyrator action was obtained also in germanium crystals by Mason, Hewitt & Wick (166) who used Hall-effect modulation to produce nonreciprocal transmission of plane-wave radiation.

Some progress has been made in determining structure on an atomic scale in solids. The methods using nuclear paramagnetic resonance [Pound (7)] and electron paramagnetic resonance [Bleaney (167)] have been particularly fruitful.

Luminescent Solids (H. W. Leverenz)

Studies of luminescence provide another potent method for gaining local information in solids [Leverenz (168); Leverenz & North (169); Hellwege (170); Larach & Turkevich (171); Bube, Larach & Shrader (172)]. Reviews of luminescent solids, in general, are given by Henderson (173) and Fonda (174). A partial review is given by Williams (175). Many studies are being made to ascertain the mechanism of "electroluminescence"; that is, luminescence emission obtained when an alternating or constant electric field, with or without electrode contact, is applied across a solid [Tetzner (176); Destriau (177); Curie (178); Piper & Williams (179); Froelich (180); Waymouth (181); Burns (182)]. The efficiency of this process is even less than that of cathodoluminescence, and the present view is that electrons are the excitants. The electrons may be injected from electrodes in contact with the solid [Haynes & Briggs (183); Newman (184); Lehovec, Accardo & Jamgochian (185)], or derived within the solid from thin-film breakdown at surfaces, or by field acceleration and avalanching of electrons already in the conduction band.

The use of phosphors for detecting high-energy particles in nucleonics research has been vigorously developed, and the status of this work is summarized by Garlick (186), Curran (187), and Birks (188).

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KINETICS OF REACTIONS IN SOLUTION[1]

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Space limitations make this review necessarily somewhat selective. Four subjects, polymerization, radiation-induced reactions, heterogeneous catalysis, and enzyme reactions, have been almost completely omitted.

Books.—More than the usual number of books dealing with solution kinetics were published in 1953. Frost & Pearson (1) have written an excellent text on kinetics which emphasizes application of kinetics to mechanisms of reactions. Volume VIII of *Technique of Organic Chemistry*, edited by Friess & Weissberger (2) deals solely with kinetics and mechanisms, primarily of reactions in solution. Ingold (3) has written a most comprehensive book on *Structure and Mechanism in Organic Chemistry*. Bartlett (4) and Waters (5) have extensive chapters in Volumes III and IV of Gilman's *Organic Chemistry*, dealing respectively with the study of organic reaction mechanisms and with oxidation processes. In both cases kinetic studies receive considerable emphasis. A 1953 Faraday Society discussion on reactivity of free radicals (6) has been published and one part deals with reactions in the liquid phase.

Theory.—There have been no major changes in either general rate theory or in theory for reactions in solution. As usual, most of the general theoretical considerations have dealt with the more amenable gas phase and are consequently considered in the following chapter of this book. Several papers have dealt with the kinetic equations for consecutive and simultaneous processes. Thus, Lautout, Wyllie & Magat (7) have solved the differential equations for the reaction sequence: $A+B=C$; $B+C=D$; $C+C=E$ for the case of excess A. Higgins & Williams (8, 9) give equations for a pair of consecutive second order steps involving a bifunctional molecule reacting with a unifunctional molecule. Perry & Pigford (10) have solved the equations for simultaneous absorption of a gas in a liquid and a second order reaction of the dissolved gas using a digital computer.

Jaffé (11) has used the molecular orbital approach to treat the problem of the transition state of Walden inversion type reactions. He believes that the method permits more straightforward estimation of geometry and energetics than does the valence bond approach. Brown (12) discusses the problem of predicting reactivities for conjugated systems and states that if there is agreement between predictions made by the method of the isolated molecule, i.e., for early stages in the reaction, and predictions made by the localized energy procedure, i.e., for a stage beyond the transition state, then

[1] The survey of the literature pertaining to this review was concluded in November, 1953.

one can have considerable confidence in the predictions. Bell & Jones (13) have done further experiments on the acid-base catalyzed iodination of acetone in order to look more carefully for the presence of a ternary or "push-pull" rate term. They do find appreciable contribution from a term of the type $k(R)(HA)(A^-)$. However, from a further analysis they claim that ternary mechanisms are not of major importance for acid-base catalyzed reactions in aqueous solutions.

Apparatus and Methods

The problem of very fast reactions is of continuing interest. Kilpatrick, Baker & McKinney (14) discuss improvements in the apparatus of McKinney & Kilpatrick (15) for rapid reactions in which gases are evolved. The procedure involves jet mixing in a time of about 2 msec. with pressure measurements by a strain gauge feeding into an oscilloscope. The apparatus has been used to study the reaction of sodium-potassium alloy with water (14). Goodridge (16) gives details of an apparatus for measuring initial rates of absorption of gases by liquids with contact times of only 10^{-2} seconds. A drop of liquid falls through the gas and the pressure change of the latter is followed by a sensitive diaphragm whose movement causes a change in capacitance. Marshall & Davidson (17) have used the flash photolysis technique to measure the rate of recombination of iodine atoms in solutions of heptane and carbon tetrachloride. For the latter solvent the second order rate constant is 0.7×10^{10} l./mol sec., which means roughly a 40-fold greater rate than that in the gas phase with one atmosphere of argon (18). This flash photolysis technique has been applied by Porter & Windsor (19) to a study of triplet state intermediates in solution. Spectra interpreted as due to a triplet state are obtained from roughly 10^{-5} M solutions of anthracene and similar molecules in hexane. The triplet states appear to have half-lives of the order of 100 μ sec. and the method seems to make it possible to study the behavior of such very short-lived species. An intriguing method which permits determination of lifetimes of fluorescent molecules with a precision of 2×10^{-10} sec. is given by Bailey & Rollefson (20). The fluorescence is excited with light modulated at high frequency by a standing ultrasonic wave in the liquid, and lifetimes are determined by measuring the phase shift between the emitted and exciting light. Freedman (21) and Manes (22), in similar developments, consider the measurements of very rapid rates of reversible reactions by ultrasonic absorption. The essence of the method is that chemical reaction can lead to excess absorption and that the frequency of the maximum excess absorption is related to the gross reaction rate near equilibrium. Freedman has applied the method to existing data (23) on ultrasonic absorption in liquid acetic acid and has calculated, for example, a rate constant for the dissociation of the dimer at 20°C. of 1.1×10^5 sec.$^{-1}$ A different and interesting possibility for measuring rates of certain fast "exchange" reactions is pointed out by Gutowsky & Saika (24), who note that a fast exchange of certain chemical species, e.g., protons, among different chemical states will lead to a single magnetic resonance line,

whereas, with slow or no exchange several lines may exist. As an example, these authors state that the data on the proton magnetic resonance of aqueous solutions of sodium and potassium hydroxide indicate that the average "exchange" lifetime of an hydroxide ion in water is 10^{-4} sec. or less. Roughton (25) and Chance (26) have written excellent descriptions of several other rapid reaction techniques, including the well-known flow procedures.

Several papers have appeared on the effects of ultrasonic waves on rates of reaction in solution. Thompson, Vilbrandt & Gray (27) have studied the effect of ultrasonics at frequencies ranging from 400 to 1500 kc. on the acid catalyzed hydrolysis of ethyl acetate. The increases in rate are only in the order of 5 per cent. Dognon & Simonot (28) discuss the effects of ultrasonics in terms of the resultant cavitation. Busnel and co-workers (29 to 32) have studied the influence of ultrasonics on the oxidation of iodide solutions by dissolved oxygen. They find a maximum in the dependence on wave length; they also note that only a small fraction of the energy is utilized for the chemical reaction. In a somewhat similar study, Loiseleur & Petit (33) show that the presence of oxygen acceptors such as hydroquinone decreases the oxidation which occurs when solutions of strychnine in the presence of air are exposed to ultrasonics. Schulz & Henglein (34) detect free radicals formed by ultrasonics by showing that acrylamide in methanol is polymerized and diphenylpicrylhydrazyl is decolorized. They find a marked effect of the nature of the dissolved gas present in the solution. Thus, reaction occurs if argon or nitrogen are present but not if hydrogen or carbon dioxide are present. Incidentally, there is a recent book by Kudryavtsev (35) on applications of ultrasonics to physical chemistry.

Caldin, Long & Trowse (36) and Caldin & Trickett (37) report on apparatus for accurate control of temperature to −80°C. They have used the apparatus to study the rate of reaction of ethoxide ion in ethanol with trinitrotoluene and with *p*-*p*′-*p*″-trinitrotriphenyl methane over the wide temperature interval of from −80° to 20°C. For both reactions the Arrhenius equation fits the data quite precisely. For these reactions the authors believe that the rate step is a proton transfer and that the good fit of the Arrhenius equation argues against any entrance of a "tunneling" mechanism which, if it occurs, might be expected to enter at low temperatures.

Page (38) gives fairly detailed design information on capacity flow reactors for kinetic studies. This technique has proved itself very useful for precision measurements and its use will doubtless expand. Grunwald (39) summarizes general aspects of this technique. An interesting, somewhat different application of the capacity flow method is given by Page (40) who uses it to establish constant concentrations of a transient ferric ion-thiosulfate ion complex and thus determine its absorption spectrum.

Nucleation

The quantitative aspects of formation of solids from fluids are now commonly treated by nucleation theories of the type originally proposed by

Turnbull & Fisher (41), and during the last year several fairly "chemical" investigations have been reported. Christiansen & Nielson (42) give a mathematical treatment which assumes that after a time all nuclei are of the same age. The results are reported to agree with data on crystal growth from aqueous salt solutions only for later times in the growth process. Thomas & Staveley (43) have studied the freezing of drops of several molecular liquids. All the liquids showed extensive supercooling and usually solidified over a quite narrow temperature range. This is assumed to indicate homogeneous nucleation. Wylie (44) has studied the freezing of very pure and deliberately contaminated water in glass and has compared the results with theory. Hirano (45) has studied the rate of crystallization from supersaturated aqueous solutions of potassium chloride and has treated the data by the Turnbull-Fisher equation. From the dependence of rate on temperature, Allen (46) concludes that crystallization of 6-6 nylon from the melt involves a nucleation mechanism and discusses the rate equation.

Applications of Isotopes

Two aspects of the use of isotopes which continue to be of interest are the relative rates of isotopic reactions and the use of isotopes as tools in mechanism studies. It is well-known that for reactions involving breaks of bonds to the various hydrogen isotopes (H, D, and T) reaction rates can differ substantially and that for isotopes of heavier atoms the "isotope effects" are much smaller although still detectable. From the theories of Bigeleisen (47) and Eyring & Cagle (48), among others, the normal expectation is that reaction will be faster for the light isotope. Thus, Kaplan & Welzbach (49) have measured the relative rates of hydrolysis of triphenylsilane-H and -T in moist piperidine and find the ratio $k_T/k_H = 0.8$ which is in good agreement with theory (47, 48). This result casts considerable doubt on the earlier report of Gilman, Dunn & Hammond (50) who stated that the deuterium compound reacts considerably faster than the protium analogue. Raaen & Ropp (51) have studied intramolecular isotope effects in reactions of benzoic α-C^{14} anhydride and have found no temperature coefficient for the isotope effect, in agreement with theory, but a sizeably larger isotope effect than theory (47) predicts. Yankwich & Stivers (52) report on the intramolecular isotope effects for the decarboxylation of malonic and bromomalonic acids and find that the C^{13} effect is about that predicted by Bigeleisen's theory, but that the C^{14} effect is about twice that predicted, i.e., the ratio of C^{14} to C^{13} effect is 3.6 rather than the calculated value of 2. Yankwich, Belford & Fraenkel (53) and Yankwich & Belford (54) give data on the C^{13}/C^{12} intermolecular isotope effects of the decarboxylation of malonic acid in concentrated sulfuric acid and in quinoline. For the former solvent, the magnitude of the effect agrees with theory. The temperature coefficient is stated to disagree with theory but the disagreement is actually not large. In quinoline there is disagreement between theory and experiment, both in the magnitude of the isotope effect and in the

temperature coefficient, and it is concluded that the decomposition is more complex in this solvent. Schmitt & Daniels (55) find that in the acid hydrolysis of urea at 100°C. the ratio of the C^{14} to C^{13} effect is 1.8, in close agreement with the predicted ratio of 1.9. From these various results it is clear that the fairly simple theory of Bigeleisen seems to fit in some cases and not in others. Two other items further complicate the picture. One is a report by Yankwich & Promislow (56) that for acetic acids of different origin the C^{13}/C^{12} isotope ratios differ, making it necessary to apply the phrase "normal isotope content" with considerable caution. The second is a suggestion by Pitzer & Gelles (57) that perhaps the C^{13} rate is really higher than should be expected due to "catalysis" by the nonzero magnetic moment of the C^{13} nucleus. The evidence in support of this is that the rate of decarboxylation of phenylmalonic acid in solution appears to be accelerated by the paramagnetic dysprosium ion more than would be expected from salt effects alone. Finally, Bigeleisen & Wolfsberg (58) consider the theory of isotope effects on rates of reactions which involve simultaneous bond rupture and bond formation.

Wilmarth and co-workers (59, 60) have used both para hydrogen and deuterium to study the exchange of dissolved hydrogen and aqueous alkali, and also hydrogen and amide ion in liquid ammonia. In both cases the exchange reactions are first order in hydrogen and in base concentration. A tentative mechanism is suggested in which, for the aqueous case, the rate determining step is $D_2+OH^-=D^-+DOH$. Fronaeus (61) has studied the heterogeneous exchange between Cd^{++} in solution and Cd in a cadmium amalgam at equilibrium potential and, from the fact that the rate is first order in aqueous Cd^{++} but independent of concentration of cadmium in the amalgam, concludes that the rate determining step is diffusion of Cd^{++} through the Nernst diffusion layer near the amalgam surface.

Studies continue on electron transfer reactions of the type $Fe^{*+++}+Fe^{+++}=Fe^{*+++}+Fe^{++}$ using isotope "labeling" to follow the reaction. Dodson (62), in an extension of previous work, gives salt effect data for the aqueous phase thallous-thallic ion exchange. The rate of the ferrous-ferric exchange is shown by Hudis & Wahl (63) to be dependent on fluoride ion concentration and the data can be explained by assuming that exchange at different rates occurs between ferrous ion and the ferric species, Fe^{+++}, FeF^{++}, FeF_2^+, FeF_3, etc. Haissinsky (64) reports a comparatively rapid exchange between Cr^{++} and Cr^{+++} ($t_{1/2}$ from 2 to 5 min.), which is quite different from the slow exchange reported by Plane & Taube (65). Two explanations suggest themselves. One is that this is a case of "induced" exchange resulting from the chromatographic separation procedure. The second is that these may really be studies with species of the type $[Cr(Cl^-)_2(H_2O)_4]^+$ and $[Cr(SO_4^=)_2(H_2O)_2]^-$ rather than with the chromic aquo ion. Fava (66) has studied the slow exchange between Pb(II) and Pb(IV) in 7 *M* KOH at 80°C. He also finds exchange between Pb^{++} (aq) and solid Pb_3O_4 but since the exchange is only partial he concludes that the lead atoms in Pb_3O_4 are not equivalent. Shep-

pard & Wahl (67) have shown that the exchange between $MnO_4^{=}$ and MnO_4^{-}, although fast, is measurable with half-times of several seconds at 1°C. and at concentrations in the order of 10^{-4} *M*. This rate is still slow relative to collision frequencies and this fact is of considerable interest because with such symmetrical species, restrictions of the Franck-Condon type have been postulated to be small (68). For all these electron transfer reactions there is uncertainty as to whether there is actual transfer of an electron through the solvent or whether the mechanism involves an atom transfer. Taube, Myers & Rich (69) have ingeniously shown that, at least in some cases, there is atom transfer. For example when $Co(NH_3)_5Cl^{++}$ is reduced by Cr^{++}, one Cl is found on the resulting Cr(III) species for every Cr^{++} oxidized. Furthermore, radioactive Cl^{-} present in the solution during the oxidation does not appear in the Cr(III) species.

In the field of organic mechanisms, Sibbett & Noyes (70) have used radioactive iodine to study mechanisms of exchange of molecular iodine with alkyl iodides and have found evidence for both radical and molecular processes. Roberts & Yancey (71) have studied the racemization of camphene-8-C^{14} and have shown that two mechanisms enter, one of which does not cause isotope-position rearrangement. From a comparison of the polymerization of normal allyl acetate with that having deuterium at the α-positions, Bartlett & Tate (72) conclude that the chain termination step involves transfer of a hydrogen atom from the α-position of allyl acetate to a radical. Gold & Long (73) have studied the rate of hydrogen isotope exchange between anthracene in carbon tetrachloride and concentrated sulfuric acid. They find that exchange is most rapid at the *meso*-positions and ascribe the strong dependent of rate on acidity to the increase in solubility of anthracene in the sulfuric acid. Several papers (74 to 77) report additional experiments on the rate of exchange between halide ions and organic halides. Work by Keefer & Andrews (78) on the exchange between organic halides and ICl gives evidence that the reaction proceeds through a 1-1 halide-ICl complex. A series of papers by Bunton, Halevi & Llewellyn (79, 80) give data on the exchange of oxygen between nitric acid and water and discuss the relation of the results to mechanisms for aromatic nitration.

Inorganic Reactions

Coordination compounds.—This active field will be aided by an excellent review by Basolo (81) dealing with stereochemistry and reaction mechanisms of hexacovalent complexes. Taube & Posey (82) give rate and equilibrium data for "inner sphere" and "outer sphere" complexes from the pair $[Co(NH_3)_5H_2O]^{+++}$ and $SO_4^{=}$. The mechanisms of substitution for reactions of octahedral complexes are treated by Pearson, Basolo, Stone & Boston (83, 84), who consider both stereochemistry and reaction mechanisms and point to the likelihood of a plurality of mechanisms. They find that for aquation of species of the type $[Co(AA)_2Cl_2]^{+}$ an increase in bulk of the

bidentate group causes an increase in rate and they interpret this as evidence for a dissociation, or SN-1, mechanism. Brown, Ingold & Nyholm (85, 86) treat this same general problem and, by studying the reactions of $[CoCl_2en_2]^+$ ion in methanol to avoid the aquation reaction, show that there is a transition from a unimolecular or SN-1 mechanism to a bimolecular or SN-2 mechanism as one goes from a weakly to a strongly nucleophilic attacking group. In order of decreasing nucleophilicity, the groups studied were MeO^-, N_3^-, NO_2^-, NCS^-, Br^-, Cl^-, and NO_3^- and the transition from SN-2 to SN-1 occurred between NO_2^- and NCS^-. These authors also discuss the steric course of the SN-1 mechanism and conclude that the quinquevalent intermediate can take up the substituting anion at comparable rates at all of the distinguishable positions. In another significant paper on this topic Bunton & Llewellyn (87) have used O^{18} as a tracer to show that in the reaction of hydroxide ions with ions of the type $[(NH_3)_5Co(OOCR)]^{++}$ there is a gradual change in bond break from Co-O to C-O as the group R varies from CH_3 to CF_3, i.e., as RCOOH becomes more acidic. As the authors point out, this clearly indicates an added complexity beyond an SN-2 mechanism.

Kinetics of racemization of optically active complex ions of ferrous and nickelous have been studied by Davies & Dwyer (88) and by Basolo, Hayes & Neumann (89). The latter group finds that the rates of dissociation and racemization of two complexes of the type $[Ni(AA)_3]$ occur at the same rate and with the same energy of activation. From this they conclude, in contrast to previous workers (88, 90), that the racemization actually goes by a dissociation mechanism. Adell (91) has studied the rate of isomerization of a nitrito Co(III) complex to the more stable nitro form. The transformation occurs in both the solid state and in dilute solution and is first order in the latter. Hamm (92) reports on the rate of *cis-trans* isomerization of $[Cr(C_2O_4)_2(H_2O)_2]^+$ and finds a first order reaction with ΔH^* of 17.5 kcal./mol. and ΔS^* of -15.3 e.u. Yalman (93) gives rates of formation and aquation of $[Co(NH_3)_5I]^{++}$ and postulates that its reduction by iodide ion goes by a one-electron transfer to give iodine atoms. Emschwiller (94) and also Asperger, Murati & Cupahin (95) have studied the kinetics of dissociation of $Fe(CN)_6^{-4}$ and its reaction with nitrobenzene. The latter group have investigated the marked Hg^{++} catalysis of the reaction. Hamm & Davis (96) find that the consecutive reactions between $Cr(H_2O)_6^{+++}$ and $C_2O_4^=$ are first order in the Cr(III) species and zero order in $C_2O_4^=$. Recent papers (97, 98, 99) consider the kinetics of exchange and substitution reactions of planar tetracoordinated complexes of platinum.

Oxidation-reduction.—Betts & Dainton (100) appear to have successfully analyzed the complex kinetics of the spontaneous bleaching of ferric thiocyanate solutions; the proposed mechanism involves the ion-radical $(SCN)_2^-$ as well as the neutral dimer $(SCN)_2$. Ashurst & Higginson (101) propose the following two-step mechanism for the Tl(III) – Fe(II) reaction

$$Tl^{+++} + Fe^{++} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Tl^{++} + Fe^{+++}$$

$$Tl^{++} + Fe^{++} = Tl^{+} + Fe^{+++}.$$

As evidence for the reversibility of the first step, they find that ferric ion retards the rate, contrary to an earlier report by Johnson (102). For the reaction of cerium (IV) and bromide ion in aqueous sulfate media, King & Pandow (103) find the rate law, $-d[Ce(IV)]/dt = (Ce^{IV})(SO_4^{=})^{-1}\{k_1(Br^-)^2 + k_2(Br^-)\}$, and give a mechanism which explains it. In chloride solutions, an activated complex of the formula $Ce(SO_4)_2ClBr^{=}$ becomes important. Neptune & King (104) report on a similar study of the reaction between selenious acid and iodide ion for which they find (and interpret) the rate law

$$-\frac{d[Se(IV)]}{dt} = \frac{(H_2SeO_3)(H^+)^3(I^-)^4}{k_1(I_3^-) + k_2(H^+)(I^-)}.$$

Duke & Borchers (105) report on the complex kinetics which enter for acidified mixtures of Ce(IV) with chloride and thallous ions. Boyer & Ramsey (106) report on the "catalysis" of the oxygen-iodide ion reaction by the simultaneous occurrence of the pervanadyl-iodide ion reaction and believe that the intermediate from the latter reaction which is responsible for the catalysis is I_2^-. Kuz'minykh & Bomshtein (107) find a somewhat analogous catalysis of the ferric ion-sulfur dioxide reaction by cupric sulfate and attribute it to a step in which sulfur dioxide reduces the cupric to cuprous.

In the complicated field of nitrogen compounds, Higginson, Sutton & Wright (108, 109) report on the oxidation of hydrazine in aqueous solution and, from experiments which include the use of N^{15} as a tracer, conclude that the reaction can involve both one- and two-electron transfer processes leading to N_2 and NH_3 in the first case but only to N_2 for the two-electron transfer. Li & Ritter (110) relate kinetics and mechanism of the reactions of nitrous acid with nitrosyldisulfonate ion and sulfonate to mechanisms for diazotization and deamination. Ramsey & Yost (111) give a complex mechanism for the ferric ion catalyzed reaction of nitrosyldisulfonate and hydroxylamine monosulfonate ions. The basic postulate is a comparatively rapid reaction between $Fe(OH)^{++}$ and the hydroxylamine sulfonate ion. Schmid & Pfeifer (112) report on the reactions of ammonium and glycinium ions with nitrous acid, usually with added halide, in solutions of nitric acid, and postulate preliminary formation of nitrosyl halides. Maschka (113) has used the same ammonium ion reaction in solutions of chloride-containing nitric acid and of sulfuric acid to arrive at hydrolysis constants for NOCl and $NOHSO_4$. Reactions of nitrous acid with iodide ion are considered by Sambasivan & Suryanarayana (114, 115). Williams & Simkins (116) have studied the kinetics of both the nitration of guanidinium ion and the reverse, denitration of nitro-guanidine in 71–83 per cent sulfuric acid. The nitration rate falls off sharply with increasing water content and it is concluded that nitronium ion is the nitrating agent. The rate of dimerization of cyanamide

in aqueous solution has been studied (117) as have the consecutive bimolecular reactions of the dimer with formaldehyde (118) and the hydration of the dimer (119).

Further aspects of the well-known reactions of hydrogen peroxide and iron salts have been studied by Taylor & Weiss (120) who give precise rate constants for H_2O_2 plus Fe^{++}, by Abel (121) who considers the mechanism, particularly the role of the HO_2 radical, and by Andersen (122) who gives a mechanism to explain the acceleration by cupric salts of the iron catalyzed decomposition of H_2O_2. Weiss (123) has reconsidered his mechanism for the autooxidation of ferrous ion and now assigns a prominent role to the ion pair, $Fe^{+++} \cdot O_2^-$. Baer & Stein (124) conclude from their studies of the decomposition of peroxide in the presence of acidified ceric sulfate that the reactions steps are

$$(a)\quad H_2O_2 + Ce(IV) \rightarrow HO_2 + H^+ + Ce(III)$$
$$(b)\quad HO_2 + Ce(IV) \rightarrow O_2 + H^+ + Ce(III).$$

In other words, they believe the OH radical does not play a role and that reoxidation of Ce(III) does not occur. Davis & Higginson (125) give evidence that the iodide ion catalyzed reaction of hydrazine and hydrogen peroxide in acid solutions is a steady state process which involves the separate reactions:

$$(a)\quad 2H^+ + H_2O_2 + 2I^- = 2H_2O + I_2$$
$$(b)\quad N_2H_5^+ + I_2 = 5H^+ + N_2 + HI^-.$$

The evidence is that the observed rates and steady-state iodine concentrations are in agreement with the values calculated from the known rate equations for the separate reactions. Incidentally, the authors doubt that a direct hydrazine-peroxide reaction occurs in neutral or alkaline solutions and believe that "trace impurities" are responsible for the reactions observed. Bogdanov (126) reports on dichromate and molybdate ion catalysis of the H_2O_2 decomposition and Beers & Sizer (127) consider both the kinetics and thermodynamics of the catalase steady-state decomposition of hydrogen peroxide.

Organic Reactions

Linear free energy relationships.—The best known of these is the Hammett (128) equation,

$$\log \frac{k}{k_0} = \sigma\rho$$

where k_0 and k refer to rate or equilibrium constants of an unsubstituted benzene derivative and of a compound substituted at the *meta-* or *para-*position of the benzene ring and σ and ρ are substituent constant and reaction constant, respectively. Jaffé (129), in a recent review, has collected a very complete list of reactions to which the Hammett equation applies, and has critically discussed many aspects of the equation and of the σ and ρ values. One of the interesting problems is that of explaining and predicting

values of σ and ρ, which, of course, were initially developed as empirical constants. As one aspect of an extensive series of papers on the theory of aromatic substitution, Sixma (130) has calculated σ values on a "localized energy" basis using data on bond lengths and bond moments; the agreement between observed and calculated values is quite good. Jaffé (131, 132) has made molecular orbital calculations of electron densities and shown that they correlate with σ values, and has also considered the calculation of ρ values. That the basic hypothesis of dependence on electron density is correct is shown by Meal's (133) correlation of σ values with nuclear quadrupole coupling frequencies (which are closely related to the location of the bonding electrons) and also by the considerations of Smith & Eyring (134) on charge distribution. However, precise calculations of σ and ρ values will probably not be possible for some time. In the meantime, the Hammett equation is being applied with increasing frequency and is being extended to other systems. One of the many examples of its application is that of Berliner & Liu (135) who show that the rates of the alkaline hydrolysis of substituted ethyl *p*-biphenylcarboxylates correlate well with σ values but that, as might be expected either from a dampening of electrostatic effects or from lack of coplanarity of the biphenyl rings, the transmission coefficient, ρ, is only about one-fourth as large as for ethylbenzoates. Kochi & Hammond (136, 137), in their study of the solvolysis of substituted benzyl tosylates, find a poor correlation of rates and σ values for the two substituents *p*-CH_3 and *p*-CH_3O and discuss reasons. Overberger & Cummins (138) have made a thorough study of the second order oxidation of *p*-*p'*dichlorobenzyl sulfide by *para*-substituted peroxybenzoic acids and find an excellent σ correlation. Of interest is the fact that for the reaction of the substituted compounds there is a sizeable change in energy of activation and also a linear increase of ΔS^* with E. Vène, Tirouflet & Pinel (139) find an excellent σ correlation of their data on rates of alkaline hydrolysis of substituted phthalides but in this case, although E changes with substituent, ΔS^* is almost constant. Bartlett & Kice (140) use the fact that rates of rearrangements of substituted benzoates of 9-decalyl hydroperoxide fit the Hammett equation with a ρ value of 1.34 as evidence that the reaction is ionic in character. Incidentally, a rather complete study of this same rearrangement in methanol and aqueous methanol solutions has been made by Goering & Olson (141). They note that the rearrangement is intramolecular and is accompanied by a concurrent solvolysis. They postulate that both the solvolysis and rearrangement result from the same ion-pair intermediate. Roberts & Moreland (142) report σ values for *m*-hydroxyl and *m*- and *p*-carbethoxyl of 0.014, +0.334 and +0.402, respectively, [see, however, Jaffé (129) for critical comment]. An important paper by Roberts & Moreland (143) shows that the effects of substituents in the 4-position of the saturated bicyclo [2.2.2.] octane-1-carboxylic acid follow an equation analogous to that of Hammett. This indicates that transmission of effects through a conjugated system is not an essential item. Roberts and Moreland also discuss critically the

alternate possibilities of inductive (or internal) and field (or general electrostatic) transmission of substituent effects.

Jaffé (129, 144) has considered extensions of the Hammett equation to some cases where there is more than one substituent. Thus, for two or more constituents on a given ring he suggests replacing the $\rho\sigma$ term by $\rho\Sigma\sigma$, implying additive effects. For the use of two or more nonequivalent rings in a given compound he proposes the equation $\log k/k_0 = \rho_1\sigma_1 + \rho_2\sigma_2 + \cdots$, implying in this case that the effects from the different rings are additive. Taft (145 to 148) has proposed some significant extensions of the Hammett equation to cases of *ortho* substituents and also to aliphatic reaction series. He suggests that for these situations there are separate polar effects (leading to σ^* values) and steric effects and, further, that the steric effects involve both "strain" and "hindrance" effects. It appears that in many cases this will be a fruitful analysis. For example, when the polar effects are small (i.e., small σ^*) Taft shows that one can utilize a steric equation

$$\log k/k_0 = \delta E_s$$

where δ and E_s are the steric analogues of ρ and σ. Swain & Scott (149) propose a two term equation for simultaneous nucleophilic and electrophilic effects on a displacement reaction,

$$\log k/k_0 = sn + s'e$$

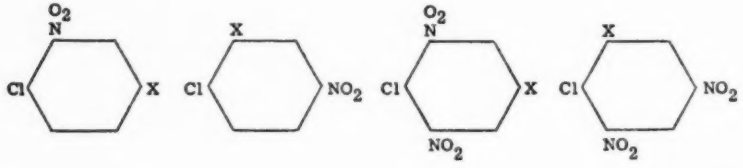
where n and e are reactivity constants for the nucleophilic and electrophilic reactants and s and s' are substrate constants (analogous to the Hammett ρ). Swain & Scott consider in particular the case where the electrophilic term can be neglected and show that the resulting limited equation can be satisfactorily applied (for a given solvent) to a large variety of reactions of nucleophilic agents with various substrates. Swain & Dittmer (150) show that solvolysis reactions of organic halides in various solvents can be correlated by the equation

$$\log\left(\frac{k}{k_0}\right)_A - \log\left(\frac{k}{k_0}\right)_{A_0} = ab$$

where A and A_0 refer to any compound and to the standard reference compound, and k and k_0 refer to rate constants in any solvent and in the reference solvent. The constant a is characteristic of the compound and b is characteristic of the solvent. It is pointed out that success of the equation is undoubtedly due to effective cancellation of kinetic energy and entropy terms. The fit for some 15 compounds and 19 solvents appears quite satisfactory.

Displacement reactions.—The classifications SN-1 and SN-2(3) for displacement reactions and also SE-1 and SE-2 for elimination reactions continue to be highly useful even though it is becoming clear that there are some real complexities involved. In an interesting extension of the effects of deuterium substitution, Shiner (151) has studied both rates of the solvolysis (SN-1, E-1) of deuterated tertiary amyl chlorides and the amount of olefin

formation (SE-1). Both methylene and β-deuteriums decrease the rate but only methylene deuteriums influence the amount of olefin. The conclusion is that the transition state for the reaction appears to be rather complex and that some "elimination type" driving forces probably enter in the rate determining step. Coburn, Grunwald & Marshall (152) have studied solvent and salt effects on the solvolysis of *s*-butyl bromide and find no evidence for a bromide ion "mass law" effect which, in their opinion, still leaves the solvolysis mechanism for *s*-alkyl halides difficult to classify. A particularly complete demonstration of an SN-1 (carbonium ion) mechanism for the reactions of triphenylmethyl thiocyanate and halides is given by Swain, Scott & Lohmann (153) who also show, by studying relative reactivities of the trityl ion for seven nucleophilic agents, that the discrimination by this ion is especially high. Hine & Brader (154) have studied the SN-2 reactivities of ethyl bromide and five of its β-substitution products with thiophenate ion and find that the rates vary with β-substituent in the order $H > C_2H_5 \sim CH_3 > Cl \sim Br \sim F$. They also give heats and entropies of activation for the reactions. Miller & Williams (155) and Heppolette & Miller (156) have continued studies on the SN mechanism in aromatic compounds and find that for substituents in the 1 position of 1-X, 3-nitro, 4-chlorobenzene, the influence of X on the rate of replacement of the chloride by OMe^- is in the order $I > Br > Cl > F \sim H$. These authors have also made similar kinetic studies on the species:



and conclude that the *ortho*-effects do not correlate well with geometric predictions. However, Brown & Berneis (157) and Brown & Bonner (158) from their study of solvolytic and quaternization reactions of neopentyldimethyl halides and amines respectively, conclude that there is a large "strain" effect resulting from the neopentyl group. In agreement with expectations, the presence of the bulky neopentyl group increases the rate of the solvolytic reactions (relative to *t*-butyl chloride) but decreases the rate of the bimolecular process (relative to *n*-butyl dimethylamine). In another study of a quaternization reaction, that of phenacyl bromides with 4-picoline in benzene solution, Brebner & King (159) find the somewhat unexpected rate law,

$$\text{Rate} = k(\text{Amine})(\text{RBr}) + k'(\text{Amine})(\text{RBr})^2$$

Hudson & Brown (160, 162) and Archer, Hudson & Wardill (161) have studied solvolysis rates of substituted benzoyl chlorides as a function of

solvent composition and substituent groups and conclude that there is a gradual transition from SN-2 to SN-1 as the polarity of the solvent increases and as the amount of electron release accumulates. In a somewhat comparable study, Robertson (163) has investigated the reaction

$$RO_3SC_6H_4X + Y = RY + O_3SC_6H_4X^-$$

where Y is a nucleophilic agent, R is an alkyl group and X is a *para*-substituent. From variations in the nucleophilicity of Y, in ionizing power of the solvent and in character of R he concludes that there are changes from SN-2 to SN-1 mechanisms somewhat similar to those observed for alkyl halides. De Le Mare & Vernon (164) show that the reaction of thiophenoxide ion with 1:1-dimethylallyl chloride goes by an SN-2′ mechanism, i.e., substitution with anionotropic rearrangement, to give 3-methylbut-2-enyl phenyl sulfide and discuss the implications of this and related results. In connection with the SN-2′ reaction, the demonstration by Stork & White (165) that the entering group comes in *cis* to the departing one is of considerable interest. Dostrovsky & Halmann (166), in a series of four papers, have made a study of both solvolysis and substitution reactions of several phosphorochloridates and phosphinyl chlorides. They find evidence only for a simple bimolecular mechanism in all cases. They find no evidence for an "expanded shell" transition complex involving *d* orbitals and conclude that there is a great similarity between the groups =POCl and —COCl.

The first order acetolysis and also the bimolecular reaction with methoxide ion of 2,2-diphenylethyltosylate and the analogous 2-phenyl-2(*p*-tolyl)- and 2,2-di(*p*-tolyl)-compounds have been studied by Burr (167). The methyl substituents increase the acetolysis rates (nonlinearly) but decrease the bimolecular rates linearly, in agreement with SN-2 expectations. By using 2-phenyl-2(*p*-tolyl) ethyl-1-C^{14} tosylate, Burr shows that there is extensive rearrangement of the *p*-tolyl group during the first order reaction and none in the second order.

Acid-base catalysis.—Bell & Pearson (168) have used rapid reaction techniques to study two proton transfer reactions, one to the anion of *p*-nitrophenol and the other from a nitramine group to aqueous ammonia. The first proved too fast to measure and the second gave at room temperature the high rate constant of 10^5 l/mol. sec. Since both reactions are ones where there was some reason to expect a slow rate, the authors conclude that proton transfer to or from oxygen and nitrogen will normally be too rapid for direct measurement. For the rather different case of the slow ionization of pseudo acids, Pearson, Dillon & Williams (169, 170) show that there is generally a good correlation between the rates and the ionization equilibria but that for two cases of bases with bulky *ortho*-groups the reaction rates with nitroethane are slower than expected. Thus, these appear to be examples of a normally unexpected phenomenon, steric effects on proton removal. Barrott, Denton & Lamberton (171) conclude that the acid catalyzed decomposition of primary nitroamines probably proceeds by

formation of NH_2NO_2 and an alkyl cation. Cohen & Hammond (172) find general acid catalysis in the benzidine rearrangement and conclude from their rate data that the transition state consists of hydrazobenzene, two protons and an anion of the acid. DeWolfe & Roberts (173) find a rather complicated general acid catalyzed hydrolysis of N,N′-diphenylformamidine and explain their results by the assumption that only the free base undergoes hydrolysis. However, it is noted that general base catalyzed hydrolysis of the conjugate acid is an alternate possibility. Kaeding & Andrews (174) find that the rate of acid catalyzed hydrolysis of a ketal in aqueous ethanol parallels the Hammett acidity function and suggest that the rate determining step involves the conjugate acid and a water molecule. However, in view of the known uncertainties (175), application of the acidity function in mixed solvents should probably be done with considerable caution. Levy *et al.* (176, 177) give precise rates and temperature coefficients for the hydration of two isomeric gaseous pentenes which lead to the same alcohol. At 50 per cent reaction there is no evidence of conversion of isomers from which they conclude that the mechanism does not involve a rapid, reversible addition of a proton to the olefins followed by slow reaction of the carbonium ion with water. McCauley & King (178) find that the decomposition of diazoacetone shows only specific hydrogen ion catalysis. Most salt effects are normal but are large for the halides and with these haloacetones are formed.

Kilde & Wynne-Jones (179) have determined the catalytic constants of the bases water, ammonia, hydroxide ion, and glucosate ion for the mutarotation of glucose. The constant for hydroxide ion is greater than predicted by the Brönsted relation, whereas, for most base catalyzed reactions it is markedly less. Ballester & Bartlett (180) find that the hydroxide ion catalyzed condensation of benzaldehyde and phenacyl chloride is first order in each of these three species, showing that enolization is not the rate determining step. Bell & Spiro (181) have studied the base catalyzed bromination of ethyl malonate under conditions where the rate varies with bromine concentration and conclude that, depending on pH, bromination involves both the anion and the enol. Bafna & Gold (182) find that the hydrolysis of acetic anhydride is strongly catalyzed by pyridine and explain the observed, rather complex kinetics by postulating that the conjugate acid of pyridine (formed from pyridine and the product acetic acid) is catalytically inactive. Gold & Jefferson (183) have extended this work by studying the catalytic activity of several amines for the hydrolysis of acetic anhydride and by studying the hydrolysis and decomposition of the mixed acetic formic anhydride. They postulate that with these anhydrides the rate determining step is transfer of an acylium group, e.g., CH_3CO^+, to the basic catalyst.

An important potential source of error for reactions in hydroxylic solvents is pointed out by Baker & Neale (184) and Caldin & Long (185) who show that reactions of the type

$$OH^- + C_2H_5OH = H_2O + C_2H_5O^-$$

can frequently cause marked changes in the constituents of a solution. Thus

even in ethanol containing two per cent water the above equilibrium is well to the right.

Oxidation.—Auto-oxidation reactions are discussed in a review article by Bawn (186) who considers mechanisms, in particular, the important role of metal salts. Mulcahy & Watt (187) have studied both the uncatalyzed oxidation of benzaldehyde by oxygen and the reaction as catalyzed by benzoyl peroxide. For the catalyzed reaction the initial rate, R, is given by $R = R_0 + k\,(Bz_2O_2)^{1/2}$, where R_0 is rate in absence of catalyst, and from this result it is concluded (*a*) that for the catalyzed reaction the chains terminate by mutual interaction, and (*b*) that the chain carriers are different for the catalyzed and thermal reactions. In the absence of inhibitors (to which the reaction is very sensitive) the initial rate of the thermal reaction is given by

$$-\frac{d(O_2)}{dt} = \frac{(RH)^2(O_2)}{b(RH)^2 + c(O_2)}.$$

This is tentatively explained by a chain mechanism with chain carriers of the types Q^* and QO_2^* and with two termination steps, $QO_2^* \rightarrow X$ and $Q^* + RH \rightarrow X$. The authors report no sign of autocatalysis (at least during the initial stages). Ingles & Melville (188) give further details on the benzaldehyde oxidation in decane solution and consider more specific chain mechanisms for both the thermal and photo-induced reaction. It seems safe to conclude that the major aspects of the mechanism for this oxidation are known even though some of the details are still uncertain. Ingles & Melville (189) also have studied the photo-induced co-oxidation of mixtures of benzaldehyde and *n*-decanal and conclude that both molecules are involved in a single, mixed chain. Dunn & Waters (190) have studied the retarding action of 15 quinones on the benzoyl peroxide initiated auto-oxidation of benzaldehyde and report that only quinones of high oxidation-reduction potential are effective. However, correlations between redox potentials and retarding ability are satisfactory only if the quinones are structurally similar. Rigg & Gisser (191) find that in the oxidation of saturated esters of adipic acid there are marked changes in rate as the amount and position of branching in the alcohol group is varied. Tipper (192) concludes that in solvents of low dielectric constant the decomposition of decalin hydroperoxide involves a homolytic rupture and a chain mechanism but that in solvents of higher D an ionic mechanism enters. Seubold & Vaughn (193) give rates and temperature coefficients for the acid catalyzed decomposition of cumene hydroperoxide in aqueous acetic acid. They believe that the reaction shows only specific hydrogen ion catalysis. Boardman (194) finds that the reduction of cumene hydroperoxide by ferrocyanide is first order in these reactants and also in hydrogen ion and concludes that there is a one-electron transfer to the ferrocyanide to give the radical $C_6H_5C(CH_3)_2O\cdot$. In contrast, Boardman & Hulse (195) believe that with iodide ion there is a nucleophilic displacement of hydroxyl ion from the hydroperoxide, i.e., a two-electron transfer.

A series of four papers gives details on the second order oxidation by perbenzoic acid of *cis*- and *trans*-azobenzenes, substituted azobenzenes, and

some related compounds [Badger, Buttery & Lewis (196); Badger & Lewis (197)]. The products are azoxy compounds. The *cis*-azobenzene is oxidized about 60-fold more rapidly than the *trans*, the difference being entirely due to a lower energy of activation. For the substituted compounds, electron release substituents at the *m*- and *p*-positions increase the rate and electron withdrawal groups decrease it. The effects of two substituents are accurately additive. The entropy of activation stays essentially constant, i.e., the effects are entirely due to changes in ΔH^*. Finally, there is an excellent correlation with the Hammett σ values. As noted earlier, Overberger & Cummins (138) in their study of the rates of oxidation of *p*-*p*-dichlorobenzyl sulfide by substituted perbenzoic acids also found a σ correlation but in this case there were compensating changes in ΔH^* and ΔS^*. Overberger & Cummins (198) have also studied the rates of oxidation of *p*-*p'*-dichlorobenzyl sulfide in isopropyl alcohol by hydrogen peroxide. The observed second order rate constant contains two terms, e.g., at 30.2° $k = 3.1 \times 10^{-5} + 3 \times 10^{-1}(H_2SO_4)$. The energies of activation are quite different for the acid catalyzed and uncatalyzed terms and it is concluded that two mechanisms are operating. Wiberg (199) has studied a rather different sort of reaction of hydrogen peroxide, the conversion of benzonitrile (and substituted benzonitriles) to benzamide in basic solution. The rate is first order in nitrile, peroxide, and hydroxide ion and it is concluded that the mechanism involves a nucleophilic attack by the ion HO_2^- on the carbon of the nitrile.

Drummond & Waters (200) have started a detailed study of stages in the oxidation of organic compounds by potassium permanganate. Initial studies were on the MnO_4^--$MnO_4^=$ stage using precipitation by barium ion to stop the reactions at the $MnO_4^=$ stage. They report that with a few exceptions all classes of organic compounds are oxidized during this stage. Later work deals with the $Mn^{+3} \rightarrow Mn^{++}$ stage for which acidified manganic pyrophosphate solution is a useful reagent. A study of the oxidation of pinacol by this reagent leads to the conclusions (*a*) that manganic-pyrophosphate-pinacol complexes are rapidly and reversibly formed, and (*b*) these break down by a one-electron transfer to give manganous ion, acetone, and a radical which in turn is rapidly oxidized by manganic ion. Thamsen (201) has studied the oxidation of formic acid by chlorine and finds the only rate step to be a bimolecular one between formate ion and chlorine. This differs from Shilov & Slyadnev (202) who reported that a reaction between chlorine and the free acid entered also. Lang & Magdalena (203) have studied the oxidation of tetramethylbenzidine by nitrous acid. The rate expression in the presence of air is, Rate $= k$ (TMB) $(HNO_2)^2$ $(H^+)^{-1}$. A mechanism to explain this is advanced which, among other things, postulates the intermediate, $H_2NO_2^+$.

Andrews & Keefer (204) report on the reaction of bromine with *t*-amyl alcohol in carbon tetrachloride solution to give trimethylethylene dibromide. The rate law is complex and is interpreted in terms of a 1:1 alcohol-bromine complex which, it is postulated, reacts with an alcohol molecule to give a

colorless intermediate. Buckles & Yuk (205) find that the reaction of crotonic acid with mixtures of bromine and tribromide ion follows the rate law, $\text{Rate} = k(C_3H_5COOH)(Br_2)(Br_3^-)$. A possible explanation is equilibrium formation of a crotonic acid-bromine complex followed by a slow reaction with the tribromide ion. Adam, Gosselain & Goldfinger (206) discuss the laws of atomic addition and substitution of halogens and show how various rate laws can result.

It is possible to discuss only a few of the many excellent papers in the recent Faraday Society Discussion (6). Melville, Robb & Tutton (207) produce trichloromethyl radicals by photolysis and then obtain absolute reaction rates of radicals with the unsaturated compounds, cyclohexene and vinyl acetate, and also with the parent molecule, bromotrichloromethane. The results are among the first for absolute rates of reaction of small free radicals in solution. Some examples are tabulated in Table I for results at 30°C. Baxendale & Magee (208) have made a quantitative study of the oxi-

TABLE I

RATE CONSTANTS FOR SOME REACTIONS OF FREE RADICALS IN SOLUTION

Reactions	k, 1. mol.$^{-1}$ sec.$^{-1}$
$CCl_3\cdot$ + Cyclohexene	256
$CCl_3\cdot$ + Vinyl acetate	1120
$CCl_3C_6H_9\cdot + CCl_3Br$	64
$CCl_3\cdot + CCl_3\cdot$	0.5×10^8

dation of benzene by the system ferrous ion and H_2O_2 and find that only phenol and diphenyl are formed and conclude that phenyl radicals do not react with hydrogen peroxide but can be reduced to benzene by ferrous ion and oxidized by ferric ion to phenol. Bawn (209) discusses the role of heavy metal ions in initiating free radical reactions and concludes that with cobalt the active entity is the cobaltic ion, or more precisely, complexes of this. As one example, to explain the cobaltous acetate catalysis of the oxidation of benzaldehyde, the rate law for which is $-d(O_2)/dt = (C_5H_5CHO)^{3/2}(Co(OAc)_2)^{1/2}$, Bawn proposes the mechanism

(*a*) $Co^{+++} + C_6H_5CHO = Co^{++} + C_6H_5CO\cdot + H^+$
(*b*) $C_6H_5CO\cdot + O_2 = C_6H_5COOO\cdot$
(*c*) $C_6H_5COOO\cdot + C_6H_5CHO = C_6H_5COOOH + C_6H_5CO\cdot$
(*d*) $2\ C_6H_5COOO\cdot$ = Termination.

Other reactions.—Cantwell & Brown (210) have studied the decarboxylation of picolinic acid in several neutral, acid, and basic (nonaqueous) solvents. The reaction is first order in all cases and slower in the acidic and basic solvents. These results lead the authors to favor a zwitterion transition state rather than a cyclic one. Incidentally, there is a pronounced correlation between ΔH^* and ΔS^* for the reaction in the various solvents, just as was

found in the authors' work with substituted picolinic acids in a single solvent (211). Schubert & Gardner (212) have studied the decarboxylation of 2-4-6-trihydroxybenzoic acid in perchloric acid solutions. The reaction presumably occurs only with the neutral molecule and is not acid catalyzed.

Overberger *et al.* (213) give the first order decomposition rates for a set of azonitriles derived from the cyclic ketones, cyclobutanone through cyclodecanone. Values of the rate, of ΔE, and of ΔS^* vary considerably with ring size. The authors give evidence that the rates measure differences in ring strain and state that "this is the first complete set of data for a free radical reaction which measures differences in ring strain." Cohen & Wang (214) have measured the first order decomposition rates of several *p*-substituted phenyl azotriphenylmethanes. The rates varied with substituents as $CH_3 \sim H > CH_3O > OH > CH_3CONH > Br > NO_2$. LeFevre & Northcott (215) have determined both the effects of *p*-substituents and of solvents on the *cis-trans* change of azobenzene. A rough correlation is found between rate and internal pressure of solvent.

Tarbell and co-workers (216, 217) report on aminolysis and hydrolysis reactions of thioacetates and also on the reaction of aniline with thiobenzoic acid in chlorobenzene, aniline, and aqueous acetic acid. In aniline the latter reaction shows the interesting rate law, $\text{Rate} = k(C_6H_5COSH)^2$, which is tentatively (but rather implausibly) interpreted as indicating a slow proton transfer between two of the acid molecules to give the conjugate acid. Noda, Kuby & Lardy (218) also report on the acid catalyzed and basic hydrolysis of several thiolesters and on their reaction with hydroxylamine. Sommer, Barie & Gould (219) find the cleavage of one methyl group from β-trimethylsilylpropionic acid in concentrated sulfuric acid to be first order in molecular sulfuric acid and conclude that the reaction goes through a siliconium ion. Eaborn (220) has studied the acid catalyzed Si-C cleavage of *p*-methoxyphenyltrimethylsilane in aqueous methanol and dioxane. The rate follows the H_0 acidity function from which the author concludes that a rapid proton transfer is involved and (more doubtfully) that the slow step is a reaction of the conjugate acid with water. Reuther (221) gives preliminary results on the aqueous hydrolysis of $HSi(OC_2H_5)_3$ and related compounds. Boozer & Lewis (222) report an interesting study on the kinetics and stereochemistry of the decomposition of optically active secondary alkyl chlorosulfites in various solvents. The reaction is first order in chlorosulfite and the rates in various solvents do not differ widely but the reported steric results vary from complete retention of configuration in dioxane to complete inversion in toluene. The mechanisms proposed all involve ionization of the S—Cl bond as the slow step. Chanley & Gindler (223) find that the pH dependence of the rate of hydrolysis of *o*-carboxynapthyl phosphates is unusual in that they are most unstable around pH = 6 and quite stable in very acidic or very basic solutions. They propose a cyclic transition state involving participation of the adjacent carboxylate group. Cherbuliez and coworkers (224 to 228) report extensively on ester formation and transformation with emphasis on phosphate esters. The second order rates of reaction

in carbon tetrachloride between iodine and a large variety of symmetrical organomercury compounds, R_2Hg, are reported by Razuvaev & Savitskii (229). There is a marked correlation of energy of activation and ΔS^* for the series, although $o\text{-}CH_3OC_6H_4$— gives an unusually large negative value of ΔS^*.

An extensive group of papers by de Jong & de Jonge (230 to 233) deals with a series of reactions between urea, formaldehyde, and various reaction products of these. Reactions of this commercially very important system have been troublesome to follow kinetically because of analytical difficulties. Using new or improved analytical procedures the authors have investigated both the addition reactions between urea (or substituted ureas) and formaldehyde to give mono-, di- and trimethylol urea and the condensation reactions which join urea fragments by a methylene bridge. Examples of these are

$$(a)\ NH_2CONH_2 + H_2CO = NH_2CONHCH_2OH$$
$$(b)\ —NHCH_2OH + H_2N— = —NHCH_2NH— + H_2O.$$

Both reactions appear to be bimolecular but type (*a*) shows general acid and base catalysis whereas type (*b*) shows only specific hydrogen ion catalysis. Rate constants and energies of activation are reported for several of these reactions.

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KINETICS OF REACTIONS IN GASES[1]

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The present trend in chemical kinetic studies is towards obtaining quantitative information of as high precision as possible. This can be achieved only because of the large amount of qualitative and semi-quantitative knowledge which is available. On the basis of this preliminary information, it is possible to design experiments with a view to discriminating between alternative mechanisms or to obtaining, unambiguously, values for specific rate constants. Attention is now being focussed on experimental methods of investigating rate processes hitherto inaccessible, often because of their extreme speed. These novel methods have been made available in many cases by the considerable advances in physics and electronics which have made possible the measurement of physical quantities with greater ease and higher precision. A considerable step forward has been achieved by the recent methods of direct observation of transient entities. The use of the mass spectrometer in detecting and estimating free radical concentrations in the gas phase is of the highest importance, but much remains to be done before this technique can be generally applied and freed from all ambiguity. Methods of generating free radicals in high concentration are now well established and a large number of free radicals have been characterized by measurements of their absorption spectra, thus making it possible to identify them and to follow changes in concentration in reacting systems. Further developments in physical methods of quantitative analysis, particularly by mass spectrometry and infrared spectrometry have made it possible to analyze products of reaction with accuracy and hence gain greater insight into the elementary processes involved.

Elementary Reactions

Reactions of atomic hydrogen.—Berlie & Le Roy (1) report an investigation of the reaction of atomic hydrogen with ethane. The hydrogen atoms are produced by thermal dissociation of molecular hydrogen on a heated filament in a flow system and detected by measurement of the heat of recombination of these atoms on a platinum or tungsten filament as described in a previous paper by Dingle & Le Roy (2). In this work, the detector is made sufficiently large so as to remove all the hydrogen atoms which reach it. In this way it is possible to follow the concentration of ethane as a function of time. The sole product in the temperature range 80° to 163°C. is methane. The course of reaction may be represented by reactions 1–4.

[1] The survey of the literature pertaining to this review was concluded in November, 1953.

$$H + C_2H_6 \rightarrow H_2 + C_2H_5 \quad 1.$$

$$H + C_2H_5 \rightarrow 2\,CH_3 \quad 2.$$

$$H + C_2H_5 \rightarrow C_2H_6 \quad 3.$$

$$H + CH_3 \rightarrow CH_4 \quad 4.$$

The primary process, reaction 1, has a rate constant given by 3.4×10^{12} exp. $(-6{,}800/RT)$ cm.^{3}/mole$^{-1}\cdot$ sec.$^{-1}$, the P factor of 4.8×10^{-3} and the energy of activation being in general agreement with values for hydrogen atom abstraction from methane by hydrogen atoms reported by Steacie & Majury (3).

Darwent & Roberts (4) have made a thorough investigation of the photochemical and thermal decomposition of hydrogen sulphide at temperatures between 27° and 650°C., and pressures between 8 mm. Hg and 550 mm. Hg. The photochemical reaction has been studied using the cadmium line at 2288 Å and the mercury band at 2550 Å. In both photochemical experiments there is reported to be a slight pressure effect, the quantum yield rising from 1.09 at 30 mm. Hg to 1.26 at 200 mm. Hg. The quantum yield using light of wavelength 2550 Å is independent of temperature but there is an increase in the production of hydrogen using 2588 Å between 500°C. and 650°C. This increase is suggested to be due to decomposition of the HS radicals formed with excess energy. The over-all mechanism is shown to be represented by reactions 5 to 8.

$$H_2S + h\nu \rightarrow H + HS \quad 5.$$

$$H + H_2S \rightarrow H_2 + HS \quad 6.$$

$$2\,HS \rightarrow H_2 + S_2 \quad 7.$$

$$2\,HS \rightarrow HS_2 + H \quad 8.$$

The thermal decomposition of H_2S is bimolecular and from energetic considerations it is suggested that the process is that represented by reaction 9.

$$2\,H_2S \rightarrow 2\,H_2 + S_2 \quad 9.$$

This reaction is heterogeneous at low pressures and homogeneous at high pressures, $E_{9\ Het.}$ is 26 kcal./mole and $E_{9\ Homo}$ is 50 kcal./mole. In a further communication, these authors photolyze H_2S and D_2S in presence of hydrocarbons (5). With olefins, the reactions which occur are 5, 6, 10, and 11.

$$H + C_3H_6 \rightarrow C_3H_7 \quad 10.$$

$$H + C_3H_6 \rightarrow C_3H_5 + H_2 \quad 11.$$

By following the rate of production of hydrogen from H_2S alone in presence of olefin, a suitable plot enables k_6/k_{10} to be obtained and knowing k_6, k_{10} may be calculated. The values found for the rate constant for ethylene and propylene addition of a hydrogen atom are in general agreement with those found by Melville & Robb (6), the agreement for propylene being very good, while that for ethylene is not so satisfactory For ethylene, $E_{10}=4.1$ kcal.

/mole, $P_{10}=0.09$ and for propylene, $E_{10}=5.0$ kcal./mole, $P_{10}=0.52$. For the abstraction reaction for propylene, $E_{11}=5.0$ kcal./mole, $P_{11}=0.1$, and for butene-2, $E_{11}=5.0$ kcal./mole and $P_{11}=0.3$. Abstraction reactions are measured using D_2S, the reaction scheme being given by reactions 12 to 14.

$$D_2S + h\nu \rightarrow D + DS \qquad 12.$$

$$D + D_2S \rightarrow D_2 + DS \qquad 13.$$

$$D + RH \rightarrow HD + R \qquad 14.$$

In this case, the production of HD is measured. For the series ethane, propane, *n*-butane, and *i*-butane, E_{14} is respectively 9.0, 7.2, 7.1, and 6.3 kcal./mole. For these, the steric factor, P_{14}, is approximately 0.6.

Allen, Melville & Robb (7) have extended previous investigations on hydrogen atom reactions with olefins, using molybdenum oxide as an efficient remover of hydrogen atoms in competition with the unsaturates. Allowance has been made for disappearance of these atoms on the walls of the vessel and it is shown that no appreciable error was introduced previously by ignoring this. Previous experimental observations have been verified and it is shown that addition of a hydrogen atom falls off in efficiency in the series C_2H_4, C_2F_4, C_2Cl_4.

Reactions of methyl radicals.—A comprehensive survey of the literature pertaining to methyl radical reactions has been produced by Trotman-Dickenson (8). In a further publication, he discusses entropy changes in free radical reactions (9). The entropy change in a reaction process can be written $R \cdot \ln(A_f/A_b) = \Delta S$, where A_f and A_b are the frequency factors for the forward and back reactions, respectively. A calculation of the entropy change involved, together with a knowledge of either A_f or A_b enables one to calculate the frequency factor of the reverse reaction. Reactions discussed are of three types, metathesis reactions, unimolecular decompositions, and free radical decompositions. A reasonable measure of agreement is reached where the calculated value may be compared with experiment. Examples are quoted of unimolecular decompositions with frequency factors differing from the normal value of about 10^{13} sec.$^{-1}$. It is suggested that these anomalous reactions are, in general, special cases as, for example, where an alkyl radical decomposes, rearrangement must also take place to form an unsaturated molecule.

The photolysis of mercury dimethyl has been studied by Rebbert & Steacie (10). Over a temperature range of 125° to 250°C., the photolysis, using a medium pressure mercury arc has a quantum yield close to unity. At 239°C., the quantum yield has risen only to 1.2. Methane is formed by reaction 15, E_{15} having a value of 10.8 kcal./mole. The only other product

$$CH_3 + CH_3 \cdot Hg \cdot CH_3 \rightarrow CH_4 + CH_3 \cdot Hg \cdot CH_2 \qquad 15.$$

of significance is ethane from the recombination of methyl radicals. Small amounts of ethylene and propylene are noted.

Ingold & Lossing (11) have studied the thermal decomposition of mercury dimethyl using a mass spectrometer to measure the methyl radical concentration. They employ a flow method, the flow tube which has a moveable furnace, being connected to the mass spectrometer ionization chamber by a tube fitted with a fine pinhole so that a sample of the flow tube contents is continuously running into the spectrometer. In this way, it is possible to obtain a measure of the methyl radical concentration. By varying the distance between the furnace and the spectrometer leak, the decay in radical concentration can be determined. It would appear that under the conditions of experiment (temperatures between 161° and 814°C. and pressure of mercury dimethyl between 4.8 and 18.5 mm. Hg) the radicals disappear by a first-order heterogeneous and a second-order homogeneous process. The second-order reaction has been investigated and is found to have a negative temperature coefficient of -2.2 kcal./mole, while the collision efficiency is about 0.028. It is suggested that the negative temperature coefficient arises by a change in the collision diameter of the methyl radical with temperature. The suggested mechanism of the disappearance of methyl radicals is that shown in reactions 16 and 17.

$$2\,CH_3 \rightarrow C_2H_6^* \qquad 16.$$

$$C_2H_6^* + M \rightarrow C_2H_6 + M \qquad 17.$$

The reactions of methyl radicals and deutero-methyl radicals with hydrogen and deuterium have been investigated by Majury & Steacie (3) over a temperature range 130° to 300°C. The radicals are produced by the photolysis of the appropriate acetone.

$$CH_3 + H_2 \rightarrow CH_4 + H \qquad 18.$$

$$CH_3 + D_2 \rightarrow CH_3D + D \qquad 19.$$

$$CD_3 + H_2 \rightarrow CD_3H + H \qquad 20.$$

$$CD_3 + D_2 \rightarrow CD_4 + D \qquad 21.$$

They find that for the reactions 18 to 21, $E_{18}=9.2$ kcal./mole, $P_{18}=0.7\times10^{-3}$; $E_{19}=11.7$ kcal./mole, $P^1_{19}=3.5\times10^{-3}$; $E_{20}=10.2$ kcal./mole, $P_{20}=2.5\times10^{-3}$; $E_{21}=10.9$ kcal./mole, $P_{21}=2.0\times10^{-3}$. It is seen that the greatest effect of isotopic substitution occurs when the molecular hydrogen is substituted, not the radical. These values depend on the constants for the reaction 22 which, for purposes of comparison, are taken here to be $E_{22}=0$

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad 22.$$

kcal./mole, $P_{22}=1$. From these results a calculated value for the reaction 23

$$H + CH_4 \rightarrow CH_3 + H_2 \qquad 23.$$

is obtained, $E_{23}=7.0\pm1.5$ kcal./mole and P_{23} between 10^{-3} and 10^{-4}.

A similar investigation by Whittle & Steacie (12), photolyzing acetone in the temperature range 130° to 420°C. in presence of H_2, HD, and D_2

agrees with the above energies of activation lying between 10 and 12 kcal./mole and steric factors of about 10^{-3}. It is pointed out that the abstraction of a hydrogen atom is approximately twice as fast as abstraction of a deuterium atom. This is discussed in terms of the intermediate transition complexes and their moments of inertia.

The photochemical decomposition of azomethane has been studied by Jones & Steacie (13) over a temperature range 24° to 190°C. using light of wavelength 3660 Å. The products are largely methane, ethane, and nitrogen, arising by reactions 24 to 26.

$$CH_3 \cdot N{=}N \cdot CH_3 + h\nu \rightarrow N_2 + 2\,CH_3 \qquad 24.$$

$$CH_3 + CH_3 \cdot N{=}N \cdot CH_3 \rightarrow CH_4 + CH_2 \cdot N{=}N \cdot CH_3 \qquad 25.$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad 26.$$

The quantum yield of nitrogen production is close to unity and independent of temperature, $E_{25} - \frac{1}{2}E_{26}$ being 7.6 kcal./mole. The inclusion of reactions 27 and 28 is necessary to account for the production of tetramethyl hydra-

$$CH_3 + CH_2 \cdot N{=}N \cdot CH_3 \rightarrow (CH_3)_2 \cdot N{-}\dot{N} \cdot CH_3 \qquad 27.$$

$$CH_3 + CH_2 \cdot N{=}N \cdot (CH_3)_2 \rightarrow (CH_3)_2 \cdot N{-}\dot{N} \cdot (CH_3)_2 \qquad 28.$$

zine. $E_{27} - \frac{1}{2}E_{28}$ is found to be 6.4 kcal./mole. The presence of methylethyl imide is also demonstrated and shown to arise by secondary radical reactions. This photolysis is a convenient source of methyl radicals and the same authors have used it to study the reaction of methyl radicals with *n*-butane and *i*-butane (14). The main reaction is that of hydrogen atom abstraction as shown in reaction 29. For *i*-butane, E_{29} is 6.7 kcal./mole and for *n*-butane,

$$CH_3 + RH \rightarrow CH_4 + R \qquad 29.$$

E_{29} is 9.1 kcal./mole. P_{29}/P_{26} is 10^{-4} and 10^{-3} for *i*-butane and *n*-butane, respectively.

Cvetanovic & Steacie (15) have investigated the photolysis of acetone in presence of HCl at room temperature and at 150°C. The addition of HCl suppresses ethane formation and favors methane formation. The reaction proceeds by 30 and 31. This is substantiated by using fully deuterated ace-

$$CH_3 + HCl \rightarrow CH_4 + Cl \qquad 30.$$

$$Cl + CH_3 \cdot CO \cdot CH_3 \rightarrow HCl + CH_2 \cdot CO \cdot CH_3 \qquad 31.$$

tone, when it is found that the methane formed is largely CD_3H. E_{30} is about 2.1 kcal./mole and P_{30} is 7.0×10^{-3}.

The addition of chlorinated methanes to photolyzing acetone has been shown by Cvetanovic, Raal & Steacie (16) to result in increased methane production. The addition of CCl_4, which increases methane formation, is assumed to do so by an acetone-sensitized decomposition of CCl_4 to form a chlorine atom which then forms HCl by abstraction of a hydrogen atom from acetone. A stationary state concentration of HCl will then be established and

gave rise to methane by reactions 30 and 31. This is further supported since the addition of ammonia inhibits the preferential methane formation by removal of HCl. With addition of $CHCl_3$ to photolyzing acetone, ammonia does not show the same inhibition of methane formation and it is suggested that in this case, reaction 32 occurs. It would appear to be a generalization

$$CH_3 + CHCl_2 \rightarrow CH_4 + CCl_3 \qquad 32.$$

that the abstraction of a hydrogen atom from chloromethanes is facilitated by progressive substitution of chlorine atoms.

The values of E_{33} determined by Volman & Brinton (17), namely 7.5

$$CH_3 + CH_3 \cdot CHO \rightarrow CH_4 + CH_3 + CO \qquad 33.$$

kcal./mole is at variance with that found by Dodd, 10.7 kcal./mole (18). It is suggested by Pritchard, Pritchard & Trotman-Dickenson (19) that Dodd's value is in error and that reaction 33 should be written as a two-stage process consisting of reactions 34 and 35.

$$CH_3 + CH_3 \cdot CHO \rightarrow CH_4 + CH_2 \cdot CO \qquad 34.$$

$$CH_3 \cdot CO \rightarrow CH_3 + CO \qquad 35.$$

Dodd suggests in reply that reaction 35 is not considered to be, in any way, rate determining since the over-all photolysis is relatively independent of added inert gases which might be expected to increase the rate of decomposition of the acetyl radical (20). He suggests that the discrepancy may arise by chain initiation by formyl radicals or hydrogen atoms arising as a result of the photolysis. It is generally agreed that the use of intermittent illumination to obtain lifetimes of reaction chains is not warranted when the nature of the radicals leading to chain termination is uncertain.

Photochemistry

The gas phase chlorination of methylchloroformate has been investigated by Brandy & Le Roy (21). The reaction is initiated by the photolysis of chlorine and proceeds by reactions 36 to 41.

$$Cl_2 + h\nu \rightarrow 2\,Cl \qquad 36.$$

$$Cl + RH_3 \rightarrow HCl + RH_2 \qquad 37.$$

$$RH_2 + Cl_2 \rightarrow RH_2Cl + Cl \qquad 38.$$

$$RH_2Cl + Cl \rightarrow RH_2 + Cl_2 \qquad 39.$$

$$RH_2 + Cl \rightarrow RH_2Cl \qquad 40.$$

$$Cl \rightarrow \tfrac{1}{2}Cl_2 \qquad 41.$$

(RH_3 denotes $CH_4 \cdot O \cdot CO \cdot Cl$)

In the liquid phase, inhibition occurs by reaction 39 but not so in the gas phase. Termination in the gas phase is by the mutual removal of two chlorine atoms in place of reaction 40 in the liquid phase. At low-light in-

tensities, reaction 41 terminates the chains in the gas phase and it is of interest to note than k_{37}/k_{41} is the same in both gas and liquid phase.

The photochemical and thermal bromination of toluene is reported by Anderson, Scheraga & VanArtsdalen (22). The bromine concentration is measured by a photoelectric absorption method. It is found that the photochemical reaction is inhibited by HBr and that bromination occurs by a chain mechanism, the slowest step being reaction 42. The energy of activa-

$$Br + RH \rightarrow HBr + R \qquad 42.$$

tion for this reaction is 7.2 kcal./mole and the steric factor 0.22. The energy of activation for the reverse reaction is calculated at 5.0 kcal./mole. From this and thermochemical data, the $C_6H_5 \cdot CH_2$—H bond dissociation energy is calculated to be 89.9 kcal./mole. This is considerably higher than that proposed by Szwarc, namely 77.5 kcal./mole (23). It is also shown that toluene molecules function as efficient third bodies in the recombination of bromine atoms.

Fowler & Beaver (24) add further information on the photochemical formation of phosgene from carbon monoxide and chlorine. They find quantum yields of the order of 10^3 to 10^4 and propose a general equation for the rate of production of phosgene as a function of the parameters involved. Rate constants are calculated for several of the reaction steps.

The photolysis of azoisopropane is shown by Durham & Steacie (25) to proceed by an excited molecule mechanism. In the temperature range 30° to 120°C. a molecule of azoisopropane, excited by absorption of 3660 Å radiation may be quenched by collision with another azoisopropane molecule, or alternatively it may decompose to give two isopropyl radicals and nitrogen. It is found that the ratio of combination to disproportionation for these radicals is 2.0, in substantial agreement with that found by Blacet & Calvert (26). These isopropyl radicals also abstract hydrogen atoms from azoisopropane, the energy of activation for this process being fairly low at 6.5 kcal./mole.

Volman & Graven (27) show the products of photolysis of di-*tert*-butyl peroxide by 2537 Å radiation to be acetone, ethane, CO, CH_4, diacetyl, and *tert*-butyl alcohol and that this decomposition initiates the polymerization of butadiene. The energy of activation for the propagation step of the polymerization is 5.8 kcal./mole. The photolysis of acetone (producing CO, diacetyl, and ethane) also initiates this polymerization with an energy of activation for propagation of 5.0 kcal./mole. Initiated by the peroxide decomposition, the rate of polymerization is linear with butadiene pressure, but when initiated by acetone photolysis, there is a maximum in the rate /pressure curve. The occurrence of this maximum is ascribed to the deactivation of excited acetone by collision with a butadiene molecule. The butadiene is an efficient methyl radical trap as is shown by the fact that no ethane is formed on photolysis of acetone in presence of butadiene. Calcu-

lated energies of activation for decomposition of the *tert*-butoxy and acetyl radicals are respectively 11.2 and 13.5 kcal./mole.

Finkelstein & Noyes (28) have decomposed diethyl ketone photochemically in presence of oxygen. Short chains occur which are believed to involve the radical $C_2H_4 \cdot CO \cdot C_2H_5$ produced probably by abstraction of a hydrogen atom from diethyl ketone by OH radicals. In the absence of oxygen, the propionyl radical decomposes with formation of CO but in presence of oxygen, CO_2 is formed instead. Acetaldehyde and propionic acid are also products of reaction. Quantum yields are given for the production of CO_2, CO, C_2H_4, C_2H_6 and for the consumption of oxygen.

Quantitative information has been obtained on the photolysis of glyoxal using 3130 Å radiation, by Calvert & Layne (29). At temperatures between 150° and 300°C. the important processes are those occurring in reactions 43 to 45:

$$(HCO)_2 + h\nu \rightarrow (HCO)_2^* \qquad 43.$$

$$(HCO)_2^* \rightarrow H_2 + 2\,CO \qquad 44.$$

$$(HCO)_2^* \rightarrow CH_2O + CO \qquad 45.$$

The relative probabilities of 44 to 45 are in the ratio 0.15 to 0.85 with a quantum yield of CO production of 1.22 and of H_2 production 0.13. The ratio of the quantum yields for hydrogen and carbon monoxide production is independent of the normal variables except temperature on which it is slightly dependent. If is further shown that no deactivation of $(HCO)_2^*$ occurs. In agreement with previous workers (30, 31) it is shown that the formyl radical does not occur appreciably in the decomposition of glyoxal.

The photolysis of diacetyl using radiation of wavelength 2654 Å has been studied by Blacet & Bell (32) over a temperature range 28° to 200°C. The products of photolysis are CO, C_2H_6, CH_4, and acetone. Quantum yields are dependent on temperature and have been measured over the range. The quantum yield of CO production varies from 0.55 at 28°C. to 3.38 at 200°C. Included in the complete reaction scheme are steps 46 and 47, for which $E_{46} = 7.1$ kcal./mole and $E_{47} = 5.6$ kcal./mole.

$$CH_3 + CH_3 \cdot CO \cdot CO \cdot CH_3 \rightarrow CH_4 + CH_2 \cdot CO \cdot CO \cdot CH_3 \qquad 46.$$

$$CH_3 + CH_3 \cdot CO \cdot CO \cdot CH_3 \rightarrow CH_3 \cdot CO + CH_3 \cdot CO \cdot CH_3 \qquad 47.$$

By using a high intensity flash source of radiation, Khan, Norrish & Porter (33) have studied the photolysis of acetaldehyde, diacetyl, and acetone. CO_2 is added to reduce the temperature produced by the high energy input to the reaction cell. The radical concentrations produced are so high that only radical-radical reactions occur, reactions of radicals with parent molecules being unimportant. Various modes of decomposition of acetaldehyde are thought to occur, leading to the formation of CH_3, $CH_3 \cdot CO$ and H. The photolysis of diacetyl forms CH_3 and $CH_3 \cdot CO$ radicals, while from acetone, the primary products of photolysis are CH_3, $CH_3 \cdot CO$, and $CH_2 \cdot CO \cdot CH_3$ radicals.

An account of the photolysis of ethyl nitrate between 45° and 128°C. is published by Gray & Style (34). This is discussed on the basis of the mechanism embodying reactions 48 to 52. It would appear that methyl radicals

$$C_2H_5 \cdot O \cdot NO_2 + h\nu \rightarrow C_2H_5O + NO_2 \quad 48.$$

$$C_2H_5O \rightarrow CH_3 + CH_2O \quad 49.$$

$$C_2H_5O \rightarrow H + CH_3 \cdot CHO \quad 50.$$

$$CH_3 + NO_2 \rightarrow CH_3 \cdot NO_2 \quad 51.$$

$$H + C_2H_5 \cdot O \cdot NO_2 \rightarrow C_2H_5 \cdot OH + NO_2 \quad 52.$$

react preferentially with NO_2 while hydrogen atoms react with ethyl nitrate.

Dacey reports a study of the photolysis of CF_3I using radiation of wavelength 2537 Å (35). Below 10 mm. Hg pressure, a quantitative yield of C_2F_6 and I_2 is obtained while at high pressures, C_2F_4 and a polymer are formed. The quantum yield varies from 0.02 to 0.13, depending on pressure, the higher yield occurring at the lower pressure. The addition of NO and metallic silver to react with CF_3 radicals and iodine atoms causes the quantum yield to rise to about 0.73 and 0.35 respectively. The proposed mechanism is by reactions 53 to 55.

$$CF_3I + h\nu \rightarrow CF_3 + I \quad 53.$$

$$CF_3 + I \rightarrow CF_3I \quad 54.$$

$$CF_3 + I_2 \rightarrow CF_3I + I$$

or

$$2\,CF_3 \rightarrow C_2F_6 \quad 55.$$

It is pointed out that in the xenon-sensitized photodecomposition of CF_4, no C_2F_6 is formed. Since reaction 55 is shown to occur, the proposed decomposition of CF_4 by Xe^* is by reaction 56.

$$CF_4 + Xe^* \rightarrow CF_2 + F_2 + Xe \quad 56.$$

The absorption spectrum of NH and NH_2 radicals has been studied by Ramsay by the flash photolysis of hydrazine (36). He finds a critical flash energy below which there is no decomposition, but above which explosion occurs. This explosion is well known as a thermal explosion. Below the critical limit, NH_2 bands are found to be present, but are weak. Above the critical limit, NH_2 and NH bands are found and 80 per cent of the hydrazine is decomposed. The proposed mechanism is set out in reactions 57 to 60.

$$N_2H_4 + h\nu \rightarrow NH_2 + NH_2 \quad 57.$$

$$NH_2 + NH_2 \rightarrow N_2H_4 \quad 58.$$

$$NH_2 + N_2H_4 \rightarrow NH_3 + N_2H_3 \quad 59.$$

$$N_2H_3 \rightarrow NH + NH_2 \quad 60.$$

At low temperatures, reactions 57 and 58 occur, but at higher temperatures induced by the higher energy flash, reactions 59 and 60 lead to chain branching and explosion. The quantum yield for decomposition is believed to lie

between 32 and 320. Addition of helium suppresses decomposition and also reduces the NH and NH_2 absorption spectra. Ramsay also describes in another publication, a method of obtaining absorption spectra of free radicals in a continuously irradiated system (37). He points out that the limitations of the flash photolysis systems arise because of (*a*) the necessity of using inert gases to minimize thermal effects; (*b*) because a stationary state is not achieved, and (*c*) because the course of reaction may be considerably modified by using high radiation intensities and, hence, high radical concentrations. He uses a 1-metre absorption cell and arranges for the light beam to traverse the cell up to twenty times. In this way, ammonia streamed through the cell and subjected the radiation of wavelength 1849 Å, gives rise to absorption bands in the region of 6000 Å due to NH_2 radicals. With cyanogen, using a path length for the spectrum-measuring radiation of four metres, the CN band at 3883 Å is seen.

Thermal Decomposition Reactions

The decomposition of nitrous oxide at 750°C. has been studied by Friedman & Bigeleisen (38) using $N^{14}N^{15}O$ and $N^{15}N^{14}O$. The nitrogen formed is found to be not equilibriated and the NO formed does not exchange with N_2O and does not catalyze the equilibration of the nitrogen. These observations are in accord with the mechanism contained in reactions 61 to 65. This

$$N_2O + N_2O \rightleftarrows N_2O^* + N_2O \qquad 61.$$

$$N_2O^* \rightarrow N_2 + O \qquad 62.$$

$$O + N_2O \rightarrow N_2 + O_2 \qquad 63.$$

$$O + N_2O \rightarrow 2\,NO \qquad 64.$$

$$O + O + M \rightarrow O_2 + M \qquad 65.$$

does not agree with the chain decomposition mechanism having nitrogen atoms as chain carriers proposed by Pease (39).

The decomposition of N_2O_5 in presence of NO at 50.5°C. has been further studied by Johnston (40). It is shown that the efficiency of added gases, A, N_2, NO, SF_6, CO_2, N_2O_5 in producing activation of N_2O_5 by a bimolecular collision is respectively 0.14, 0.23, 0.30, 0.32, 0.40, and 1.00. A calculation of the mean lifetime of $N_2O_5^*$ gives an answer close to 10^{-7} sec. These experiments have been made at pressure of reactants of 0.08 mm. Hg and pressures of added gases 0.02 to 10 mm.Hg.

The fast reaction of nitric oxide with nitrogen pentoxide has been investigated by Cowan *et al.* (41). They employ an infrared absorption method of following the reaction, whereby they scan a selected portion of the spectrum repeatedly and rapidly, so following the concentration of NO_2 and N_2O_5. The mechanism is that in reactions 66 to 68. Rate constants are meas-

$$N_2O_5 \rightarrow NO_2 + NO_3 \qquad 66.$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \qquad 67.$$

$$NO + NO_3 \rightarrow 2\,NO_2 \qquad 68.$$

ured, k_{66} being 0.042 sec.$^{-1}$ and k_{67}/k_{68} being approximately 0.036. By enriching NO_2 with N^{15} and adding it to N_2O_5, exchange occurs and the N_2O_5 acquires N^{15}. This is suggested to be confirmation of the existence of the back reaction 67.

A publication by Kassel (42) examines the known data on the decomposition of nitrogen pentoxide in presence of nitric oxide in the light of his theory of unimolecular reactions. He shows the comparison of theory with experiment to be satisfactory for this reaction. However, it is further shown that the theory does not give a satisfactory interpretation of the decomposition of nitrous oxide.

The thermal decomposition of nitric acid above 400°C. is the subject of a publication by Johnston, Foering & Thompson (43). Above this temperature, reaction is found to be homogeneous in glass vessels. It is inhibited by NO_2 but unaffected by the addition of water and oxygen. The initial first order character is sustained by the addition of NO, CO, and H_2 and it is believed that these function by removal of OH radicals, so preventing the back reaction with NO_2. The mechanism is given by reactions 69 to 72.

$$HNO_3 \rightleftarrows OH + NO_2 \qquad 69.$$

$$OH + HNO_3 \rightarrow H_2O + NO_3 \qquad 70.$$

$$NO_3 + NO_3 \rightarrow NO_2 + O_2 + NO \qquad 71.$$

$$NO + NO_3 \rightarrow 2\ NO_2 \qquad 72.$$

The rate constant for the forward reaction 69 is approximately 0.3 sec.$^{-1}$.

By decomposing diethyl peroxide in presence of nitric oxide and ethyl nitrite, Levy finds that the ethoxyl radical reacts more rapidly with the NO than with the ethyl nitrite (44). This work, done at 181°C. leads to a modification of the scheme for the decomposition of alkyl nitrites in the manner indicated in reactions 73 to 76. At low pressures, reaction 75 is favored, while

$$C_2H_5 \cdot O \cdot NO \rightleftarrows C_2H_5 \cdot O + NO \qquad 73.$$

$$C_2H_5O + C_2H_5O \rightarrow C_2H_5OH + CH_3 \cdot CHO \qquad 74.$$

$$C_2H_5O \rightarrow CH_3 + CH_2O \qquad 75.$$

$$2\ CH_3 \rightarrow C_2H_6 \qquad 76.$$

at high pressures, reaction 74 becomes increasingly important.

The decomposition of 1,4-dichlorobutane between 673° and 727°K. is shown to be first order by Williams (45). The products are HCl and butadiene. Reaction is inhibited by propylene by decreasing the rate and increasing the induction period, thus indicating a radical mechanism. The induction period decreases and rate constant increases with increasing pressure. For the unimolecular decomposition the rate constant is $10^{14.36}$ exp $(-56{,}500/RT)$. A similar mechanism is suggested for the decomposition of 1,1,2-trichloroethane at 715°K. which is partly unimolecular decomposition and partly a chain process.

Another study of the decomposition of chlorohydrocarbons has been

made by Howlett (46). The unimolecular decomposition of 2,2-dichloropropane at 370°C. to HCl and monochloropropene has a rate constant given by $10^{11.90} \exp(-43{,}900/RT)$. 1,1-dichloropropane gives similar products at 410°C. by a unimolecular process and by a chain process which can be suppressed by *i*-butene. The first-order rate constant is $10^{12.76} \exp(-51{,}200/RT)$. These pre-exponential factors are discussed in terms of energy accumulation in the decomposing molecules. In the pyrolysis of ethylidine dichloride, the addition of inert gases to restore first-order character to the reaction is discussed and it is shown that the efficiency of the added gas increases with reactivity and structural complexity.

A careful study of the unimolecular decomposition of a large number of alkyl bromides has been made by Green *et al.* (47). The decomposition takes place by a chain process and by a unimolecular process involving the splitting off of a molecule of HBr. It is found that the chain process can be suppressed by the addition of cyclohexene which is said to be more effective than the more customary propylene. In this way, the decomposition can be restricted to the unimolecular process for which the frequency factor and the energy of activation can be determined. The frequency factors for the whole series of alkyl bromides studied are close to 10^{13} and it is shown that energies of activation for the decompositions are for primary, secondary, and tertiary alkyl bromides respectively about 50, 46, and 42 kcal./mole.

Ladacki & Szwarc (48) report a study of the pyrolysis of monobromoaryl compounds in presence of toluene. The primary and rate-determining step is the scission of the C—Br bond. Frequency factors, where measured, are close to 10^{13} sec.$^{-1}$. The effect of structure of the aromatic part of the molecule on the C—Br bond dissociation energy is discussed and from the heat of formation of the phenyl radical, various bond dissociation energies of the type Ph-X are calculated. The effect of substituents on the C—Br bond dissociation energy of substituted bromobenzene has also been investigated. The effect of the nature of the substituent as well as its position in the aromatic ring is discussed.

The first order decomposition of nitromethane over a temperature range 420° to 480°C. is shown to have a rate constant of $2.7 \times 10^{13} \exp(-50{,}000/RT)$ sec.$^{-1}$ by Hillenbrand & Kilpatrick (49). A flow method is used in which the nitromethane is injected from a mechanically controlled syringe into a stream of nitrogen which then carries the vapor into a furnace. The exit stream from the furnace is analyzed for nitromethane by a polarographic method. It is found that rates are variable if the apparatus is flushed with dry nitrogen but are reproducible if wet nitrogen is used. The energy of activation quoted above is close to that required to break the CH_3—NO_2 bond. It is, however, pointed out that for short contact times there is a high yield of formaldehyde which falls off with increasing contact time which might suggest that an intramolecular process occurs, leading to the formation

of formaldehyde. The rate constant determined here is in general agreement with previous estimates in static systems.

Atkinson & Trenwith (50) have studied the thermal reactions of tetrafluorethylene over a temperature range 300° to 800°C. Below 600°C., the main reactions are 77 and 78. For these reactions, $k_{77}=1.03\times10^{8}$ $\exp(-25{,}000/RT)$ $1\cdot\text{mole}^{-1}\cdot\text{sec.}^{-1}$ and $k_{78}=8.9\times10^{15}$ $\exp(-74{,}000/RT)$

$$2\ C_2F_4 \rightarrow \text{cyclo-}C_4F_8 \qquad 77.$$

$$\text{cyclo-}C_4F_8 \rightarrow 2\ C_2F_4 \qquad 78.$$

sec.^{-1}. The value of k_{77} is in agreement with that found by Lacher, Tompkin and Park (51) and it may be significant that the steric factor is similar to that for the dimerization of ethylene to butene found by Pease (52). At temperatures in the region of 600° to 800°C., the chemistry becomes very complex, the products being saturated and unsaturated fluorocarbons in addition to high molecular weight tars.

A study of the thermal decomposition of ethylene oxide, propylene oxide, dimethyl ether, and dioxane has been made by Lossing, Ingold & Tickner (53) with a view to identifying the intermediate free radicals. These molecules have been decomposed in the temperature range 650° to 1100°C. in a flow system, the products of the pyrolysis being determined by mass spectrometric analysis of the gas stream. By subtracting the spectrum of known molecular constituents, the residual spectrum can be assigned to the free radicals present. It is found, for instance, that each molecule of ethylene oxide gives rise to 0.6 methyl radicals while for propylene oxide, this is lower at 0.36 methyl radicals. Dimethyl ether gives rise to large amounts of methyl radicals and dioxane gives a small yield of methyl radicals. Formaldehyde is also shown to be a long-lived intermediate in the decomposition of dimethyl ether. By adding nitric oxide to the flow system, the collision efficiency for the interaction of a methyl radical with NO is calculated to be 2×10^{-4} at 950°C. This agrees with other estimates at temperatures ranging from 25°C. to 800°C., suggesting a low or zero activation energy for this reaction. The collision efficiency for the recombination of two methyl radicals is found to be 2.5×10^{-2} in general accord with the accepted values. This work has been extended by Lossing & Ingold (54) in a further publication in which benzene derivatives have been pyrolyzed in the same apparatus. The compounds studied are benzene, toluene, benzaldehyde, anisole, diphenyl, phenyl ether, and benzyl ether. The products in general consist of H_2, C, and hydrocarbons. The aromatic radicals phenyl and benzyl have been detected in fair amount and have a reasonable stability below 1150°C. The oxygenated radicals are not found in such abundance, possibly on account of lower thermal stability.

In a series of papers, Ashmore & Chanmugam (55) discuss the reactions involved in the system H_2, Cl_2, NO and NOCl at temperatures of the order

of 300°C. The reactions involved are those given by equations 79 and 85.

$$NO + Cl_2 \rightarrow NOCl + Cl \qquad 79.$$

$$NOCl \rightarrow NO + Cl \qquad 80.$$

$$Cl_2 \rightarrow 2\ Cl \qquad 81.$$

$$Cl + H_2 \rightarrow HCl + H_2 \qquad 82.$$

$$H + Cl_2 \rightarrow HCl + Cl \qquad 83.$$

$$Cl + NOCl \rightarrow NO + Cl_2 \qquad 84.$$

$$H + NOCl \rightarrow NO + HCl \qquad 85.$$

The production of HCl is explained on the basis of a nonbranching chain sequence in which initiation occurs by reaction 79. The rate constant for reaction 82 is found to be 4.8×10^8 $1 \cdot mole^{-1} \cdot sec.^{-1}$ at 250°C. with an energy of activation of 5.5 kcal./mole. The rate of decomposition of NOCl is found to be faster at 250° to 300°C. than expected for the bimolecular process involving two molecules of NOCl which occurs at lower temperatures. It is proposed that at these elevated temperatures, NOCl decomposes by reactions 80 and 84. It is found that the addition of chlorine to the reaction mixture accelerates this decomposition, thus supporting the inclusion of reaction 84. It is further calculated that $k_{79} = 4 \times 10^9 \exp(-20{,}300/RT)$ $1 \cdot mole^{-1} \cdot sec.^{-1}$.

The reactions of chlorine atoms, produced by flash photolysis of Cl_2, with oxygen have been studied by Porter & Wright (56). At room temperature the ClO radical is found and its concentration has been followed with time by absorption spectrum measurements. They find the initial reactions

$$Cl + O_2 \rightarrow Cl{\cdot}O{\cdot}O \qquad 86.$$

$$Cl + Cl{\cdot}O{\cdot}O \rightarrow 2\ ClO \qquad 87.$$

to be 86 and 87. The rate of removal of chlorine atoms forming Cl_2 and ClO is 46 times as fast as that of the recombination of chlorine atoms to Cl_2 in presence of nitrogen. The succeeding reaction 88 and 89 is relatively slow, bimolecular with respect to ClO and independent of total gas pressure. The rate constant for this is given as $7.2 \times 10^4 \epsilon_S \exp(0 \pm 650/RT)$ $1 \cdot mole^{-1} \cdot sec.^{-1}$, where ϵ_S is the molar extinction coefficient for ClO at 2577 Å.

The decomposition of *n*-butane in presence of oxygen (concentration less than 25 per cent) has been studied at temperatures in the region of 500°C. by Appleby *et al.* (57). The primary products are butene and water. The effect of added oxygen is well marked; for instance, the decomposition of butane is accelerated 100 times by the addition of 0.5 per cent oxygen, and carbon monoxide appears in the products. It is suggested that the function of the oxygen is in hydrogen atom abstraction to form HO_2, the reactions of the resultant alkyl radicals with the hydrocarbon being responsible for the rest of the decomposition. The over-all energy of activation is found to be 21 kcal./mole. A KCl coating on the vessel produces little effect although a pyrex vessel seemed to promote peroxide formation.

Chilton & Gowenlock (58) report the photolysis of diisopropyl mercury in a flow system at 230° to 280°C. The products arising from the interaction of NO with the isopropyl radical are shown to be 2,nitrosopropane and acetoxime, the latter arising from the former by isomerization.

Oxidation Reactions

The oxidation of ethylene and propylene has been studied by Burgoyne & Cox (59) in the temperature range 300° to 600°C. and at pressures of the order of 1 to 4 atmospheres. Experiments in pyrex vessels indicate the formation of higher olefins and aldehydes as well as CO and CO_2. These hydrocarbon products are not found in mild steel vessels under comparable conditions although here they reappear at higher pressures. It is believed that the ferrous surface promotes oxidation of these products to CO_2 and water. No such profound effect is found in stainless steel vessels.

A study of the intermediate products of oxidation of propylene is reported by Mulcahy & Ridge (60). During the induction period, which lasts for about 30 min. at 290°C., the formaldehyde concentration rises steadily after about 50 per cent of the induction period has passed, while higher aldehydes and peroxides increase in concentration only at the end of this period. The subsequent fast reaction is in accord with the view that degenerate chain branching occurs mainly by the higher aldehydes, not by formaldehyde or peroxides. This view is convincingly supported by the addition of formaldehyde and acetaldehyde to the reaction at the beginning. Formaldehyde has a small effect on the induction period but acetaldehyde in small amount reduces the induction period markedly.

Gray (61) shows that the oxidation of ethane in a flow system at 1 atmosphere and temperature 500° to 700°C. exhibits the phenomenon of periodic cool flames. A variety of surfaces has been used and variations made in the reaction vessel size and in contact time. The products are C_2H_4, CH_4, H_2, CO, CO_2, aldehydes, acids, and peroxides. It is suggested that the periodic nature of the process arises from the interdependence of reactions 90 to 93.

$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2 \qquad 90.$$

$$C_2H_5 + HO_2 \rightarrow C_2H_4 + H_2O_2 \qquad 91.$$

$$H_2O_2 \rightarrow 2\ OH \qquad 92.$$

$$OH + C_2H_6 \rightarrow H_2O + C_2H_5 \qquad 93.$$

The slow oxidation of cyclopropane has been the subject of study by McEwan & Tipper (62). At a temperature of 410°C. the over-all kinetics suggest a free radical chain mechanism with delayed branching. The products are mainly CO and water with small amounts of CO_2, CH_4, and H_2. The main intermediate is shown to be formaldehyde which rises to a maximum concentration at maximum rate. The addition of formaldehyde decreases the induction period but has no effect on the maximum rate. A full reaction scheme is given in which formaldehyde arises from the decomposi-

tion of cyclopropyl-peroxyl radicals ($C_3H_5O_2$) and chain termination occurs by wall destruction of HO_2.

Small & Ubbelohde (63) have attempted to initiate oxidation chains involving paraffins at low temperatures by starting an aldehyde oxidation chain in presence of the paraffin. These aldehyde oxidations can be accomplished at temperatures of the order 150° to 250°C. and it was hoped that the chain carriers would interact with the paraffin and so establish the paraffin oxidation process. However, this is shown not to be the case, the addition of paraffin molecules to an aldehyde oxidation resulting in inhibition of this process. This is attributed to the alkyl radicals produced from the paraffin being sufficiently unreactive that they become stabilized by decomposition to an olefin. A range of paraffins has been studied and it is shown that the inhibiting efficiency increases with increasing chain length in the series pentane, hexane, heptane. Further, *iso*pentane is more efficient than *n*-pentane, presumably on account of the lower energy required to rupture the tertiary C—H bond. The higher efficiency of 2-pentene is similarly explained in terms of the low energy required to break the C—H bond on the α-methylene group. These effects are discussed in terms of vibrational coupling along the paraffin chain.

Thomas (64) has studied the oxidation of glyoxal by NO_2 at temperatures between 160° and 210°C. The reaction is homogeneous and the rate is proportional to the pressure of NO_2 and of glyoxal, the rate constant for the over-all process being given by $10^{8.9}\exp(-19{,}800/RT)$ $1 \cdot \text{mole}^{-1} \cdot \text{sec.}^{-1}$. The products are NO, CO_2, CO, H_2O, and glyoxylic acid. The kinetic measurements are interpreted in terms of reactions 94 to 98. It is also suggested that

$$(CHO)_2 + NO_2 \rightarrow C(O)\cdot CHO + HNO_2 \qquad 94.$$

$$C(O)\cdot CHO + NO_2 \rightarrow C(OO)\cdot CHO + NO \qquad 95.$$

$$C(O)\cdot CHO + NO_2 \rightarrow 2\ CO + HNO_2 \qquad 96.$$

$$C(OO)\cdot CHO + NO_2 \rightarrow CO_2 + CO + HNO_2 \qquad 97.$$

$$C(OO)\cdot CHO + (CHO_2) \rightarrow C(O\cdot OH)\cdot CHO + CO\cdot CHO \qquad 98.$$

a similar radical mechanism can explain the oxidation of formaldehyde by NO_2 which has been interpreted by Pollard & Wyatt (65) in terms of a molecular mechanism. Further, it is claimed that this mechanism explains the oxidation of acetaldehyde by NO_2 by modification of the scheme suggested by McDowell & Thomas (66) in which HNO_2 was involved in an acid-forming process.

The reaction between NO_2 and alcohols has been investigated by Fairlie, Carberry & Treacey (67). The over-all reaction is of third order and may be written as in equation 99. The rate of the forward reaction is measured by a

$$2\ NO_2 + R\cdot OH \rightleftarrows HNO_3 + RONO \qquad 99.$$

photoelectric method. The rate constant for the forward reaction, and the equilibrium constant have been measured for a series of five alcohols. With

methanol, the energy of activation for the forward reaction is said to be −16 kcal./mole. It is also reported that this reaction is subject to autocatalysis and that a surface catalyzed reaction also occurs. The reactivity of the alcohols decreases in the order primary, secondary, tertiary and increases with increasing carbon chain length.

In a preliminary communication by Nightingale, Cowan & Crawford (68) a description is given of a fast infrared absorption method which has been used to follow the fast reaction of NO_2 with ethyl alcohol. The relevant portion of the spectrum is scanned at the rate of 10 to 20 times per second. The progress of reaction can be followed in this way and is shown to be complete in a few seconds.

The oxidation of ethylene by NO_2 is shown by Cottrell & Graham (69) to be homogeneous, the progress of reaction being described by $-d(NO_2)/dt = k(NO_2)^{1.5}(C_2H_4)^{1.2}$. The products are CO_2, CO, NO, an oil and carbon. The suggested mechanism is shown to start by addition of $2NO_2$ to ethylene, forming dinitroethane which then decomposes to form completely oxidized products. The reaction is complicated and mechanisms are ambiguous when deduced from measurements of pressure change alone.

The oxidation of a series of *n*-paraffins from propane to nonane by N_2O has been studied at 550°C. by Smith (70). The reaction is a chain process involving alkyl radicals and is inhibited by NO and by the products of reaction, almost certainly olefins produced by pyrolysis. The initiating mechanism is stated to occur by reactions 100 and 101. It is observed that the

$$R_1R_2 \rightarrow R_1 + R_2 \qquad 100.$$

$$R + N_2O \rightarrow RO + N_2 \qquad 101.$$

rate of reaction increases from methane to heptane and then decreases for octane and nonane. This is tentatively explained by increasing resonance with increase in length of the carbon chain, the radicals produced from the higher hydrocarbons having a relatively greater chance of decomposing by a unimolecular process to lower hydrocarbons.

A study of the radical reactions of NO in flames in announced by Adams, Parker & Wolfhard (71). Various combustion systems are discussed and it is shown that NO reacts with atoms and radicals in these flames. For example, in a NO-H_2 flame, reaction occurs between H and NO; in NH_3-NO flames, NO interacts with NH and NH_2 radicals and in hydrocarbon flames, interaction occurs with CH and C_2 radicals.

Norrish gives a general review of methods of producing and studying explosions initiated by flash photolysis (72). The method depends on the rapid production of a concentration of radicals coupled with a simultaneous rapid increase in reactant temperature to a value above the critical explosion limit. This may, in favorable cases, be achieved by absorption of radiation by one or more of the reactants or alternatively by introduction of a sensitizer such as Cl_2, Br_2, or NO_2. Spectroscopic investigation subsequent to the initiation can then give information concerning the nature of the inter-

mediates in the reaction and from a study of the variation of their concentrations with time, a picture of the complex process may be built up. The value of this method is illustrated by reference to experiments on the hydrogen-oxygen and acetylene-oxygen reactions. It is further shown that the explosion conditions give rise to radical concentrations far higher than can be obtained by normal flash photolysis. This enables radical spectra to be measured where no other method is adequate. So far, no spectrum has been observed which might be interpreted as being due to the very important HO_2 radical.

A study of the combustion of acetylene is described by Norrish, Porter & Thrush (73). The reaction is initiated by the flash photolysis of a small amount of NO_2, acting as sensitizer. The absorption spectra, of OH, CH, C_2, C_3, CN, and NH are found. Immediately after the flash, OH appears. This is followed by rapid chain branching involving all diatomic molecules. With excess of oxygen, the OH radical concentration rises further with total consumption of other radicals. Radicals then decay relatively slowly. It is shown that the addition of water vapor reduces the induction period by taking part in the chemistry of the process as also does CO_2. Nitrogen behaves as an inert gas. The mechanism of the combustion is discussed in some detail.

A mass spectrometric investigation of atoms and free radicals in flames is described by Foner & Hudson (74). The flame is allowed to impinge on a gold diaphragm which has a pinhole, through which a sample of the flame gases can pass into a molecular beam system and hence into the ionization chamber of a mass spectometer. By chopping the molecular beam mechanically and applying a system of phase detection to the ion beam collector which in this case is an electron multiplier, the spectrum of the beam components can be separated from the background spectrum. The flame pressures are low, of the order of 6 to 12 cm. Hg. In the hydrogen-oxygen flame, H, O, and OH are identified. From the methane-oxygen flame, stable intermediates include C_2H_2, CO, CH_2O or C_2H_6, CH_4O and C_4H_2, CH_3 radicals are also observed. In a subsequent communication, the same authors put forward evidence for the detection of HO_2 radicals from experiments of the interaction of atomic hydrogen with oxygen, the atomic hydrogen being produced by a discharge method (75). The detector is again a mass spectrometer and the spectrum peak at $m/e = 33$ occurs in such a way as to arise almost certainly from HO_2 radicals. Roughly one per cent of hydrogen atoms produced are detected as HO_2. The OH radical is also found and is believed to arise from reaction 102.

$$HO_2 + H_2 \rightarrow H_2O + OH \qquad 102.$$

The effect of surfaces on the slow combustion of methane has been studied by Hoare (76). The importance of the nature of surfaces in combustion processes is well known and each worker adopts his own standard treatment in order to attain some measure of reproducibility. This paper describes the effect of various pretreatments, e.g., heating in vacuo or in oxygen, water

vapor or carbon monoxide; pyrolysing methanol; coating with PbO or surface aging with HF. These different treatments give rise to different kinetic schemes. It is suggested that HF aging followed by several warming-up runs each day leads to good reproducibility as does the use of a PbO coating which does not require warming-up runs.

Hoare & Walsh (77) discuss the effect of PbO coating of reaction vessels on the slow combustion of methane. They show that at 500°C., the over-all energy of activation for the maximum rate of increase of pressure rises from the normal 25 kcal./mole to 58 kcal./mole in the PbO coated vessel. There is, however, no effect on the induction period. It is suggested that the effect of the coating is to destroy efficiently the HO_2 radical. The subsequent oxidation of formaldehyde is shown to occur not by interaction with a radical,

$$H{\cdot}CHO + O_2 \rightarrow HO_2 + H{\cdot}CO \qquad 103.$$

but rather by reaction 103.

A paper by Chamberlain, Hoare & Walsh (78) discusses the combustion inhibition by lead tetraethyl in terms of the formation of PbO. It is shown that inhibition occurs by suppression of degenerate chain branching perhaps by destruction of HO_2 on the PbO coating. It is also suggested that radicals such as H, OH, and O can also be destroyed. The normal HO_2 radical surface destruction given by reaction 104, may, in presence of PbO, be modified to

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad 104.$$

exclude hydrogen peroxide as a product.

Reactions Involving Energy Transfer

There are two main methods of studying the transfer of energy from one chemical species to another. The first is by a study of unimolecular reactions at low pressures where the first-order rate constant falls off due to failure to maintain the Maxwell-Boltzmann distribution of energy. The effect of added unreacting gases in restoring this distribution permits an estimate to be made of the efficiency of energy transfer in the system. The second method of study is by measuring the effect of various "third bodies" in atom and radical recombination reactions, since the "third body" which can readily accept the energy of recombination will facilitate the reaction. Both these methods have been adopted in a number of publications.

Pritchard, Sowden & Trotman-Dickenson (79) have studied the unimolecular isomerization of cyclopropane to propylene at 490°C. Reaction is homogeneous and unimolecular down to 0.007 cm. Hg pressure, the rate constant falling by a factor of 10 as the pressure is decreased from 8.4 to 0.007 cm. Hg. The shape of the curve for $\log k/k_\infty$ as a function of log pressure is compared with various theories of unimolecular reaction and the results are in good agreement with the Kassel theory (80) in which the more energetic molecules are assigned a greater rate of reaction. The efficiency of a number of added gases in restoring the energy distribution at low pressures is determined and it is concluded that simple molecules are less efficient than

cyclopropane, but more complex molecules are of comparable efficiency. This suggests that internal energy transfer occurs on each collision with complex molecules, but less often when the molecules are simple. This conclusion is further supported by an investigation by the same authors of the unimolecular decomposition of cyclobutane (81). This leads to essentially the same conclusions as does the investigation of the isomerization of cyclopropane.

The recombination of iodine atoms has been the subject of three papers. These investigations have all been achieved by using a high intensity flash to dissociate the iodine, the recombination then being studied by subsequent measurement of iodine molecule concentration by absorption methods of high resolution in time. Christie, Norrish & Porter (82) find that the rate of recombination is accurately proportional to the square of the iodine atom concentration and the first power of the concentration of the "third body." They show that where the "third body" is He, Ne, A, Kr, Xe, the rate constant for recombination has values of 1.73, 1.86, 2.42, 3.41, 3.44×10^{-32} $ml.^2molecules^{-2}sec.^{-1}$. They show that these results are in agreement with the classical kinetic theory of termolecular collisions and also with the theory of Wigner (83).

Russell & Simon (84) have studied the recombination of iodine atoms in presence of some 29 added gases. For helium as third body, they find the rate constant is 0.97×10^{-32} $ml.^2molecules^{-2}sec.^{-1}$ in good agreement with that given above. They also find that the energy of activation for recombination is -2 kcal./mole. There is a remarkable variation of the recombination constant with change of the third body. For example, with mesitylene, the recombination rate constant rises to 224×10^{-32} $ml.^2molecules^{-2}sec.^{-1}$. They consider that the perturbing field round the third body is of the Van der Waals type and using the boiling point of the additive as a measure of this field, it is shown that there is a reasonable correlation between the logarithm of the recombination constant and the boiling point of the added third body.

Marshall & Davidson (85) in a similar investigation show that the recombination constant is 4.2, 58, and 65×10^9 $1^2\cdot mole^{-2}\cdot sec.^{-1}$ when the "third body" is respectively argon, neopentane, and *n*-pentane. They suggest that a "sticky" collision occurs between an iodine atom and the "third body" which increases the efficiency of reaction. From their data, they calculate the frequency factor for reaction 105 where M is argon, nepentane and *n*-

$$I_2 + M \rightarrow I + I + M \qquad 105.$$

pentane. A_{105} has values respectively 1.1×10^{13}, 1.6×10^{14}, and 1.8×10^{14} $1\cdot mole^{-1}\cdot sec.^{-1}$. They point out that these values are larger than might be expected for such a reaction.

Reactions of Active Nitrogen

Winkler & Schiff (86) discuss the reactions of active nitrogen, produced by a discharge, with methane, ethane, propane, ethylene, and propylene.

With the paraffins, the reaction product is exclusively HCN. The reaction mechanism is given by either reactions 106 and 107, or alternatively by

$$RH + N \rightarrow RN + H \qquad 106.$$

$$RN \rightarrow R_1 + HCN + H \qquad 107.$$

$$RH + N \rightarrow R_1 + HCN + H_2 \qquad 108.$$

reaction 108. R_1 then reacts with N to form HCN and other products. With olefins, hydrocarbons are formed in addition to HCN, the reaction sequence

$$R \cdot CH = CH_2 + N \rightarrow R \cdot \underset{\diagdown\, N \,\diagup}{CH{-}CH_2} \rightarrow R \cdot CH: + CH_2N \rightarrow RCH: + H + HCN \qquad 109.$$

being as shown in reaction 109. Products arise which indicate dehydrogenation by hydrogen atoms. For methane and ethane, E_{106} is respectively 11 kcal./mole and 7 kcal./mole. For propane, E_{106} is less than 2.5 kcal./mole. For ethylene and propylene, E_{109} is less than 2.5 kcal./mole. The steric factors are all in the region 10^{-2} to 10^{-4}. It is concluded that it is reasonable that active nitrogen should be identified with the nitrogen atom.

Gesser, Luner & Winkler (87) show that the reactions of active nitrogen with butenes follow as indicated in reaction 109. In this case, the R·CH: radical rearranges to propylene which interacts with another atom of nitrogen to form HCN, ethylene, and a hydrogen atom. The main products are HCN, propylene, and ethylene with small amounts of saturated hydrocarbons and hydrogen. The order of reactivity for the butene isomers is butene-1 > *cis*-butene-2 > isobutene. Increase of temperature increases the rate of reaction for butene-1 and *cis*-butene-2, but has no effect for isobutene.

Versteeg & Winkler (88) have reinvestigated the reaction of nitrogen atoms with ethylene. Previous investigations reported formation of a polymer, but it is shown that this polymer formation can be eliminated by preventing the access of water vapor. The formation of ethane, acetylene, and hydrogen occurs by hydrogen atom reactions with ethylene or by reactions of methyl and methylene radicals formed in the course of reaction. It is also reported that cyanogen is formed and a possible method of production is discussed. The same authors have also followed the reaction of nitrogen atoms with acetylene (89). The products of reaction are HCN and an insoluble nitrogen-containing polymer. It is suggested that this polymer is formed by polymerization of a complex C_2H_2N and that hydrogen is subsequently lost from the polymer by radical attack.

Miscellaneous Reactions

Batzold, Luner & Winkler (90) have investigated the products arising from passage of an electric discharge through hydrogen peroxide in a flow system. The products depend on the trapping temperature, water, hydrogen, and oxygen resulting from the gas phase process while peroxide appears at trap temperatures below −120°C. Trapping below −150°C. leads to prod-

ucts which evolve oxygen on warming. A point of note is that identical products arise from the passage of a discharge through water vapor and by the interaction of atomic hydrogen with oxygen in a cold trap.

Maybury & Koski (91) have examined two exchange reactions of diborane. With deuterium and diborane at 25° to 75°C., reactions 110 to 112

$$B_2H_6 \rightleftarrows 2\ BH_3 \qquad 110.$$

$$BH_3 + D_2 \rightarrow BH_2D + HD \qquad 111.$$

$$BH_2D + B_2H_6 \rightarrow B_2H_5D + BH_3 \qquad 112.$$

occur. The order of the exchange reaction is 3/2 with respect to diborane and at high pressures, zero order with respect to deuterium. At low pressures, the order is first with respect to deuterium. This variation is attributed to reaction 111 being heterogeneous, the amount of surface coverage determining the rate. At high pressures, the energy of activation is 20.4 kcal./mole for the exchange process over-all. Reaction 113 has also been investigated

$$B_2H_6 + B_2D_6 \rightarrow 2\ B_2H_3D_3 \qquad 113.$$

and is homogeneous, with an energy of activation of 21.8 kcal./mole. Here again, the order is 3/2. The mechanism of this exchange is given by reactions

$$B_2H_6 \rightleftarrows 2\ BH_3 \qquad 114.$$

$$B_2D_6 \rightleftarrows 2\ BD_3 \qquad 115.$$

$$BH_3 + B_2D_6 \rightarrow BH_3{\cdot}BD_3 + BD_3 \qquad 116.$$

$$BD_3 + B_2H_6 \rightarrow BH_3{\cdot}BD_3 + BH_3 \qquad 117.$$

114 to 117. Reactions 116 and 117 are rate determining.

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PROPERTIES OF MACROMOLECULES IN SOLUTION

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Introduction

During recent years considerable work has been carried out on the physical chemistry of high polymeric systems. Accordingly, any attempt to review this subject for even one year must necessarily be limited in scope, since a complete review would require too much space. Since the subject of polymer chemistry has been receiving so much attention, failure to include many important topics in this review does not mean that those same topics have been neglected. During the past year there appeared an excellent book by Paul J. Flory, *Principles of Polymer Chemistry* (1). Except for the most recent researches of 1953, Flory's book effectively summarizes the significant polymer work of years past.

The present review will be restricted to the following topics: (*a*) Theoretical calculations of molecular size; (*b*) Viscosities of polymer solutions; (*c*) Osmotic pressures; (*d*) Sedimentation and diffusion; (*e*) Light scattering from polymer solutions. All of these topics are, of course, closely related at the theoretical level since each requires some understanding of polymer configurations. As the theories of solution behavior become more refined, ever increasing emphasis is put upon the physical structure of the polymer molecule itself. For this reason, the question of size and shape of a coiling type polymer molecule is of paramount importance, and a fuller understanding of that subject should facilitate even greater advances in theories of solution behavior. It seems appropriate, therefore, that the first topic to be treated here be concerned with the question of molecular sizes and shapes. The literature survey for this review was completed in December, 1953.

Theoretical Calculations of Molecular Size

The calculation of molecular size of a coiling type polymer molecule, such as a molecule of rubber, is a statistical problem that has attracted the attention of numerous investigators. It was proposed a number of years ago by Kuhn (2) that an approximation to the molecular size and its distribution could be obtained from the so-called random walk model. From this model one deduces that the end-to-end separation of a coiling molecule has precisely the same mathematical form as the distance travelled by a colloid particle subject to Brownian motion. In addition, one is able to predict a Gaussian distribution of molecular lengths, a distribution which is frequently used for describing molecules in solution and in the rubber-like state.

The simple random walk is deficient as a model for a polymer because it does not exclude multiple occupancy of the various sites in space. (This

objection does not apply, of course, to Brownian motion.) Specifically, it is impossible for any two atoms in a polymer chain to occupy the same space and for this reason the Kuhn model breaks down. To amend this deficiency, numerous investigators have endeavored to take into account this excluded volume effect, or, in other words, to calculate the end-to-end separation (henceforth called the "length") while taking cognizance of the sizes of the individual chain segments.

It can be shown from the simple random walk model that the mean square length is proportional to the number of links. Assuming bond angles of 90° and completely free rotation about all of the bonds, the expression governing the mean square length of a molecule of n links is simply:

$$\langle r_n^2 \rangle_{av.} = nL_0^2 \qquad \text{I}$$

when L_0 is the length of a bond. For bond angles other than 90° or for systems with restricted rotation, the equation assumes a slightly different form, namely:

$$\langle r_n^2 \rangle_{av.} = nAL_0^2 \qquad \text{II}$$

where A is a constant depending upon the bond angles, extent of any restriction on rotation, etc. The important thing to bear in mind, however, is that the mean square length, according to the random walk model, remains proportional to the number of links in a chain, at least for large n, regardless of bond angles and restrictions as to rotations about the bonds.

When one takes into account the fact that atoms or chain segments occupy space, it is quite conceivable that the functional form expressing the dependence of length upon n will depart from that represented by equations I and II. One school of thought has held that the only effect of volume exclusion for large values of n is to increase the value of the constant A. A second group adheres to the belief that $\langle r_n^2 \rangle_{av.}/n$ does not approach a limit as n becomes infinite, but that it diverges.

Hermans, *et al.* (3, 4, 5) have discussed the problem at some length using a first-order perturbation method as their basis for calculation. They recognize that for the unrestricted random walk, the probability distribution of chain lengths is subject to a differential equation identical in form to that for diffusion or heat flow. Assuming that the restricted walk must be modified in a manner determined by the gradient of the segment density in the neighborhood of a chain end, it is possible to set up a modified partial differential equation for the length distribution. The modified equation exhibits a departure from that applicable to the unrestricted walk by the presence of some additional terms which can be regarded as a perturbation. Assuming the solution to the unrestricted problem to be a first approximation, a second approximation to the mean square length can then be calculated by appropriate mathematical operation of the perturbation on the first approximate solution. The net result of such a calculation is that the form expressed by equation II is retained for large values of n, although the numerical value of

A is changed. A similar treatment has been carried out by Wall (6) with substantially the same results. When applied to the one dimensional problem, however, Wall's treatment gave an answer that fell short of the correct one, suggesting that the method may not pay enough attention to the effect of the excluded volume.

Other investigators, such as Bueche (7), James (8), and Zimm, Stockmayer & Fixman (9), have expressed a view more or less consistent with that expounded by Flory (10) several years ago. In essence these investigators say that the total number of possible interactions in the unrestricted problem giving rise to disallowed configurations is proportional to the square of the number of segments in the chain. Now, if a linear dimension of a coiled chain were proportional to $n^{1/2}$, it follows that the volume would be proportional to $n^{3/2}$. The number of interactions per unit volume would then be proportional to the quotient of n^2 by $n^{3/2}$, that is to say, proportional to $n^{1/2}$. It can then be argued qualitatively that the number of possible interactions keeps increasing with polymer size, thus requiring the polymer to grow larger than might be expected on the basis of any simple random walk picture.

An argument counter to the above is that the concentration of segments or atoms in a polymer sphere should vary inversely as $n^{1/2}$, which would mean that for high enough values of n, the average density of polymer segments can be made to approach zero. This suggests that the only factors contributing to increased polymer size would be short range interferences, which are mathematically equivalent to a simple modification of a bond angle or a restriction upon the rotation about a bond. On this basis, it is concluded that the asymptotic functional form for the mean square end-to-end separation of a coiling type polymer molecule would be that expressed by equation II with an appropriately modified A.

James has properly pointed out that an essential difference between the treatment of Hermans (and of Wall) as distinguished from his own, is the presence or absence of a normalizing factor used in calculating the numbers of allowed configurations. The underlying argument can be illustrated simply in the following way. Consider a two-dimensional random walk confined to a square lattice with mandatory right angle turns. After three steps are taken, there are two fundamentally different configurations possible, namely:

Upon making the fourth step, the two above configurations give rise to four patterns as follows:

Of these patterns, A_1 is ruled out and hence there remain only three allowed patterns, A_2, B_1, and B_2, which should be given equal weight. However, if one takes the point of view of a traveler making the walk, it might be argued that A must always be followed by A_2 since A_1 is disallowed. This would have the effect of doubling the weight of A_2, thus tending to lower the calculated mean length. This is the kind of error introduced when one normalizes to unity the probability of going somewhere from every possible configuration. The correct approach, as pointed out by James, calls for attaching equal weight to each of the allowed configurations, which cannot be done by normalizing at each step the probability of success.

One of the present authors has repeated the first-order perturbation calculation taking into account the above argument and has found, as have others, that one can thus predict divergence of the ratio $\langle r_n^2 \rangle_{av.}/n$ in three dimensions. However, one also predicts a too rapid divergence for the one and two dimensional problems, thus implying an over-correction. It appears that the first-order perturbation method undercorrects the excluded volume effect when one normalizes the walk probabilities and overcorrects when one takes into account the more rapid loss of possible configurations.

In summary, the present state of affairs with respect to the convergence or divergence of the ratio $\langle r_n^2 \rangle_{av.}/n$ is still unsettled since no positive proofs have yet appeared. The present authors (11) have endeavored to learn more about this problem by a quasi-experimental means using an electronic digital computer, but the results, though extremely interesting and useful in many respects, have still not provided a final answer to the exact effect of the excluded volume on macromolecular dimensions.

Viscosities of Polymer Solutions

Solution viscosities have long been used for characterizing high polymers, particularly their molecular weights. The original Staudinger equation, which involved a simple proportionality between molecular weight and intrinsic viscosity, has given way to numerous modifications of increased complexity. Although an intrinsic viscosity is not easily interpreted, the relative ease with which it can be measured has amply justified the theoretical study of its significance.

The actual determination of intrinsic viscosities has become more precise in recent years. The use of various empirical equations for carrying out extrapolations to zero concentration and, more recently, extrapolations to zero rate of shear have become quite common. The effect on viscosity of concentration and shear rate was reviewed in last year's *Annual Review of Physical Chemistry* by Ferry (12). Additional papers on the effect of shear rate have been published by Schurz (13) and by Sharman, Sones & Cragg (14), who noted that the effect of shear rate is most pronounced in good solvents and that it increases with molecular weight.

The well-known relationship:

$$[\eta] = KM^a \qquad \text{III}$$

where $[\eta]$ is the intrinsic viscosity, M the molecular weight, and K and a empirical constants, still remains most useful for viscometric molecular weight determinations. Several recent papers have been concerned with the precise evaluation of K and a for various polymer-solvent systems. Immergut, Schurz, & Mark (15) have published a thorough study of the intrinsic viscosity of cellulose in cupriethylenediamine solution, and Newman, Loeb, & Conrad (16) have estimated K and a for nitrocellulose in ethyl acetate, determining the molecular weights by means of sedimentation and diffusion data. In these papers, it was found that $a \approx 1$, suggesting that cellulose derivatives are "free-draining" molecules. A recently published *Symposium on Molecular Weights of Cellulose* effectively reviews the important subject of the behavior of cellulosic materials in solutions (17).

In addition to being used for molecular weight determinations, viscosity measurements are now being employed for estimating molecular dimensions, such as the end-to-end separation of a coiling type molecule. The Debye-Bueche theory (18), the Kirkwood-Risemann theory (19) and the Flory-Fox theory (20) are those most frequently used for this purpose. The Flory-Fox theory involves an expansion factor, α, which is equal to the ratio of an average molecular dimension to what that dimension would be if the molecule were an unrestricted random coil. Their theory predicts an end-to-end separation that increases with molecular weight more rapidly than $M^{0.5}$. Further details of these various theories are given in the reviews of Ferry (12) and of Immergut & Eirich (21), who give an up to date comparative criticism of the several theories.

Krigbaum & Flory (22) recently summarized the older experimental results and also presented new data on polystyrene and polyisobutylene fractions for testing the Flory-Fox viscosity theory. The viscosity of a polymer in a "poor" solvent at the critical miscibility temperature, θ, where the second osmotic virial coefficient vanishes is found to obey very well the predicted relationship:

$$[\eta]_\theta = KM^{1/2}. \qquad \text{IV}$$

However, the theory is not supported in its entirety by viscosity measurements in "good" solvents. The theory predicts that:

$$[\eta] = KM^{1/2}\alpha^3 \qquad \text{V}$$

where

$$(\alpha^5 - \alpha^3)/M^{1/2} = 2C_M\psi_1(1 - \theta/T). \qquad \text{VI}$$

In this expression, C_M is a constant for a given polymer-solvent pair and ψ_1 is an entropy parameter. Moreover, the quantity $(\alpha^5 - \alpha^3)/M^{1/2}$ should be independent of molecular weight. However, when experimental values of $(\alpha^5 - \alpha^3)/M^{1/2}$ were plotted against log M, curved plots were obtained, indicating some dependence on molecular weight. Krigbaum & Flory conclude

that equations V and VI do not provide a completely accurate description of viscosities in "nonideal" solvents, but are the best available at present.

Mandelkern & Flory (23), in extending the Flory-Fox viscosity theory to cellulose derivatives, reached the conclusion that the cellulose chain is much less rigid than is commonly supposed. This was criticized by Doty, Schneider & Holtzer (24) (as noted in the discussion of light scattering below); but more recently, Newman & Flory (25), after completing a further investigation of cellulose derivatives, reported that the theory becomes applicable to cellulosic materials only for higher molecular weights. They observed that calculated values of the "universal" constant, Φ, given by the equation:

$$\Phi = [\eta]M/\langle r_u^2\rangle_{av}. \qquad \text{VII}$$

are lower than the value, 2.5×10^{21}, calculated for most polymers, but that this value is approached with increasing molecular weight. Thus, the low molecular weight cellulose derivatives are greatly extended, but the relative degree of extension diminishes as the molecular weight becomes larger. This conclusion, which was also reached by Immergut, Schurz, & Mark (15), is in general accord with the prevailing picture of the cellulose molecular chain.

Nukushina & Sakurada (26) and Schulz (27) have recently derived theoretical equations for the viscosity of a polymer molecule in solution. Nukushina and Sakurada assumed a model between that of a rigid sphere or ellipsoid and a flexible chain; Schulz found that an equation based on a rodlike model most nearly reconciled molecular dimensions calculated from viscosity data with light-scattering results.

Experimentally, coil diameters calculated by one or another of the viscosity theories are in general found to be proportional to M^a with a greater than 0.5, except for "ideal" solutions as noted by Krigbaum and Flory. For example, Schulz & Meyerhoff (28) calculated coil diameters of polymethylmethacrylate fractions using the Kirkwood-Risemann and Debye-Bueche theories and obtained good agreement with light-scattering values. They observed that coil diameters were proportional to $M^{0.6}$, which is in agreement with values given by Fox & Flory (29). Although the exponent is greater than that predicted from unrestricted random walk theory, it is not conclusive support for one or the other of the alternatives arising from approximate theories of the excluded volume effect.

Moore & Russell (30) tried to relate the intrinsic viscosity of cellulose acetate in a wide variety of solvents to solvent power as measured by the volume of precipitant (hexane or tolene) required to precipitate the polymer from solution. The dependence of intrinsic viscosity on solvent was found to be much less than that observed for a flexible molecule, so it was concluded that cellulose acetate is relatively extended even in poor solvents. In addition, from the types of curvature observed in plots of η_{sp}/c versus c, Moore & Russell concluded that the solvation of cellulose acetate is a complex phenomenon.

Takeda & Tsurata (31) studied the temperature variation of the intrinsic viscosity of polyvinyl chloride in cyclohexanone, nitrobenzene, and dioxane. The intrinsic viscosity in the first two solvents was observed to decrease as the temperature increased and this was interpreted as a decrease in molecular size as thermal agitation overcame hindered rotation.

Polyelectrolytes constitute an interesting class of materials which exhibit remarkable behavior because of their charges. The viscosities of polyelectrolytes usually obey the Fuoss relation (32):

$$\eta_{sp}/c = A/(1 + Bc^{1/2}) + D \qquad \text{VIII}$$

in which A, B, and D are constants and c is the concentration. This was verified, for example, by the investigations of Mathews (33) on the viscosity behavior of chondroitinsulfuric acid (a polysaccharide) and of Saini (34) on polymetaphosphates. Conway & Butler (35), on the other hand, observed that the Fuoss equation was valid for thymonucleic acid and polymethacrylic acid when the viscosities were measured in a capillary viscometer, but not in a Couette viscometer, in which η_{sp}/c always increased with concentration. It was suggested that this difference might be related to different rates of shear and to the effect of shear on solution rigidity arising from particle interaction. In this connection, it should be noted that Katchalsky & Sternberg (36) have stressed the importance of correcting to zero rate of shear when measuring the molecular weights of polyelectrolytes.

Callanan & Carroll (37) have noted that there are two types of sodium thymonucleate solutions: those that are easily precipitated by alcohol and those that are not. The observed viscosities are described by different expressions, thus indicating a chemical difference dependent on ionic interactions in the two types of solutions.

Pfanstiel & Iler (38) have used viscosity measurements to examine the properties of potassium polymetaphosphates in relation to the ratio of potassium to phosphorus in the polymer. The specific viscosities of these products were shown to be sharply dependent on this ratio. A peak value for intrinsic viscosity, observed at a potassium-phosphorus ratio just less than unity, was considered to be a result of crosslinking of the polymer during polymerization.

Viscosity measurements are also being used to estimate the degree of branching of branched chain polymers. The most complete treatment of this subject is that of Wales, Marshall & Weissburg (39), who have derived an equation based on the Flory-Fox viscosity theory by including a factor involving the ratio of the radii of branched and unbranched polymer chains. Their expression was applied to the study of branching in dextran with results compatible with those obtained by means of periodate titrations.

Cragg & Brown (40) and Cragg & Fern (41) have also published a method for the viscometric detection of branching, involving the use of Huggins' equation (42):

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c + \cdots . \qquad \text{IX}$$

In the study of GR-S (butadiene-styrene copolymer), it was reported that k' remained constant for linear polymers but increased as branching occurred. The degree of branching was related to the extent of conversion and temperature during polymerization.

However, Cleverdon, Laker & Smith (43), in studying various polystyrene samples, found that Huggins' constant, k', varied over a wide range, just as if the solvent were being changed. This was attributed at least partially to the presence of polar groups (originating presumably from polymerization catalysts). These workers point out that the use of k' to detect polymer branching is uncertain if the variation of k' is the result of two separate factors, namely, branching and the presence of polar groups.

Finally, van der Wyk & Schmorak (44) have used plots of $\ln \eta_r/c$ versus c to demonstrate that animal (tunicate) cellulose is highly branched and that bacterial cellulose is slightly branched. The slopes of these plots were positive, as is the slope for branched chain amylopectin, in contrast to the negative slopes one obtains when normal linear vegetable cellulose and amylose are examined.

Osmotic Pressure

Osmotic pressure measurements on solutions of macromolecules are of interest primarily because they can be used for the determination of number average molecular weights, $\overline{M}_n$. However, solutions of macromolecules depart so markedly from ideality that considerable attention has been directed toward understanding the reasons for those departures, with particular reference to dependence on structure. The ideal van't Hoff osmotic pressure law, namely:

$$\pi = RTc/M \qquad \text{X}$$

where π is the osmotic pressure, c the concentration of the solution, and M the molecular weight of the solute, has been modified through application of the Flory-Huggins theory of polymer solutions to:

$$\pi/c = RT/\overline{M}_n + RTd_1(1/2 - \mu)c/M_1d_2^2 + RTd_1c^2/3M_1d_2^3 + \cdots \qquad \text{XI}$$

where d_1 and d_2 are densities of solvent and solute, M_1 is the molecular weight of the solvent and μ is a solute-solvent interaction constant. Equation XI predicts a linear plot of $\pi/c - RTd_1c^2/3M_1d_2^3$ versus c with an intercept equal to $RT/\overline{M}_n$ and a slope equal to $RTd_1(\frac{1}{2} - \mu)/M_1d_2^2$, from which values of μ can be calculated.

Equation XI can be regarded as a power series expansion of π/c which, in general, might be written as:

$$\pi/c = RT/\overline{M}_n[1 + \Gamma_2c + \Gamma_3c^2 + \cdots] \qquad \text{XII}$$

where Γ_2 and Γ_3 are proportional to the second and third virial coefficients. Experimental data can be fitted to equations of this type by empirical evaluation of the coefficients. In practice, terms beyond Γ_3c^2 are neglected.

Recently, Flory & Krigbaum (45) developed a new statistical treatment of very dilute high polymer solutions; they assumed that such solutions consist of two domains, the first containing polymer molecules with associated solvent, and the second consisting of pure solvent. This modified picture of a polymer solution represents a departure from the original Flory-Huggins theory, in which it was assumed that the polymer segments and solvent molecules were evenly distributed throughout the solution.

Flory and Krigbaum's treatment gives rise to an expression like equation XII for the osmotic pressure. The second virial coefficient is related to solute-solvent interaction but the third virial coefficient, which depends on interactions involving three molecules, is more difficult to obtain. Assuming the molecules to be "hard spheres," Flory and Krigbaum obtained the result:

$$\Gamma_3/\Gamma_2^2 = 5/8 \qquad \text{XIII}$$

so that:

$$\pi/c = RT/\overline{M}_n[1 + \Gamma_3 c + (5/8)\Gamma_2^2 c^2 + \cdots] \qquad \text{XIV}$$

Thus, a plot of π/c versus c should be nonlinear. Flory and Krigbaum's derivation also leads to the conclusion that Γ_2 is dependent on the molecular weight of the polymer and upon molecular weight heterogeneity (see below). Finally, they predicted that the slopes, and hence the curvatures of these plots, will be larger in good solvents than in poor solvents.

Stockmayer & Casassa (46), realizing that the "hard sphere" approximation used by Flory and Krigbaum is not a realistic molecular model, obtained a relationship for "soft" molecules, predicting a dependence of the value of Γ_3/Γ_2^2 on the expansion factor, α, derived from viscosity data. It was predicted that Γ_3/Γ_2^2 should be in the neighborhood of 0.25 or less. When this result was compared to a limited amount of published osmotic pressure data (47, 48, 49), satisfactory agreement was sometimes obtained. Although experimental values of Γ_3/Γ_2^2 were below calculated values for some of the data, Stockmayer and Casassa nevertheless felt that their estimate for Γ_3/Γ_2^2 was an improvement over the value calculated by Flory and Krigbaum. Flory (50) concurs that a value of $\Gamma_3/\Gamma_2^2 = \frac{1}{4}$ is to be preferred to a value of $\frac{5}{8}$ and thus equation XIV can be written in the form:

$$(\pi/c)^{1/2} = (RT/\overline{M}_n)^{1/2}[1 + (\Gamma_3/2)c]. \qquad \text{XV}$$

An evaluation of the applicability of the various theoretical equations to experimental data requires a review of recent experimental results. In general, the following trends are observed: Some, but not all, plots of π/c versus c show a simple linear relationship and are fitted by equation XII, with the $\Gamma_3 c^2$ term omitted. Some examples are polyvinyl acetate in ethyl acetate, polyvinylxylene in benzene, polyacenaphthalene in benzene, all studied by Masson & Melville (51), and nitrocellulose in ethyl acetate as examined by Newman, Loeb & Conrad (16), who also observed that the second virial coefficient is dependent on $\overline{M}_n^{-0.3}$. Linear results were also obtained by Hook-

way & Townsend (52) who examined various polymers (polymethylmethacrylate, polyvinylthiolactate, polystyrene, and several others, all in benzene solution) using membranes of polyvinyl alcohol. They claim such membranes are satisfactory, even for solute molecular weights as low as 2000, since they observed a close agreement between osmotic pressure molecular weights of low molecular weight polymers (a polystyrene and a phenol-formaldehyde resin) and cryoscopic molecular weights of the same materials. In a succeeding paper (53), this work was followed up by a statistical analysis which disclosed no improvement in obtaining molecular weight through use of the more complex equations such as the Flory-Krigbaum expression. It is to be noted that linear experimental results were obtained by Hookway and Townsend in a "good" solvent, benzene. These results are at variance with others which yielded curved relationships for the same or similar solutions, and also do not agree with the Flory-Krigbaum theory which predicts curvature for good solvents. Krigbaum & Flory (54) have noted, however, that the range of $(\pi/c)/(RT/\overline{M}_n)$ in the data of Hookway and Townsend is quite limited and so they feel that these results are not a fair test of the theory.

From other experimental data, nonlinear relationships of π/c versus c have been obtained. With these results, it becomes necessary to decide which of the various theoretical equations is the most satisfactory. There appears to be no final answer to this question at present and the papers in the literature are divided on the subject. For example, McLeod & McIntosh (55), using alkali-swollen cellulose membranes, examined the osmotic pressure of polyvinyl acetate in five different solvents: acetone, benzene, methyl ethyl ketone, chloroform, and ethyl acetate. When π/c was plotted versus c, curves were obtained in all cases. McLeod and McIntosh, by least-squares curve fitting, came to the conclusion that an unrestricted quadratic equation better expressed their data than the Flory-Huggins equation which did not possess enough curvature or the Flory-Krigbaum equation which gave too much curvature. Krigbaum & Flory (56), on the other hand, suggest that McLeod and McIntosh have attempted to fit their osmotic pressure data over too wide an osmotic pressure range, i.e., $(\pi/c) > 3RT/\overline{M}_n$ and prefer the use of the more restricted equation XV with $\Gamma_3/\Gamma_2^2 = \frac{1}{4}$.

Masson & Melville (51) also obtained curved plots of π/c versus c for polyvinyl acetate in benzene, polymethylmethacrylate in benzene, and polyacrylonitrile in dimethylformamide.

Fox, Flory & Bueche (57) took various osmotic pressure data from the literature, namely, Flory's earlier osmotic pressure data for polyisobutylene in cyclohexane (47), Massen and Melville's data described above, and Schick, Doty & Zimm's data on unfractionated polystyrene in cyclohexane and ethyl acetate (48). They were able to fit all these data by means of equation XIV and to obtain values of Γ_2 dependent on molecular weight. In addition, they were able to obtain a linear plot with slopes equal to Γ_2 when $(\pi/c)/(\pi/c)_0 - (\frac{1}{6})\Gamma_2^2 c^2$ was plotted against c.

Krigbaum & Flory (54) have since reported a new experimental investi-

gation of osmotic pressure. After noting that their osmotic pressure theory, as now summarized by equation XV, also predicts that the second virial coefficient decreases with increasing molecular weight and increases with molecular weight heterogeneity, Krigbaum and Flory studied the osmotic pressure relationships of solutions of fractionated polyisobutylene and polystyrene. They obtained curved plots of π/c versus c, calculated number average molecular weights, and successfully fitted the plots by means of equation XV.

In Flory and Krigbaum's theory of dilute solutions, there is a function dependent on molecular weight:

$$F(X) = 1 - X/2!2^{3/2} + X^2/3!3^{3/2} - \cdots \qquad \text{XVI}$$

where X depends on the expansion factor, α:

$$X = 2(\alpha^2 - 1) \qquad \text{XVII}$$

which, in turn, is dependent on the molecular weight. Flory and Krigbaum relate the second virial coefficient to $F(X)$ as follows:

$$\Gamma_2 = M(\bar{v}^2/V_1)(\psi_1 - \kappa_1)F(X) \qquad \text{XVIII}$$

where $\bar{v}$ is partial specific volume of the polymer, V_1 is the molar volume of solvent, and ψ_1 and κ_1 are entropy and enthalpy parameters.

When Γ_2 is calculated from viscosity measurements by means of these equations, there is obtained only an approximate fit to the experimental data, though the molecular weight dependence exists and the order of magnitude is correct. The predicted variation of Γ_2 with heterogeneity is smaller than that observed experimentally, but appears to be qualitatively correct.

As noted in the next section, Schulz & Meyerhoff (58) have shown from diffusion and sedimentation data obtained for acetone solutions of polymethylmethacrylates that the second virial osmotic coefficient is strongly dependent on molecular weight, in line with Flory and Krigbaum's theory.

The same polystyrene used by Hookway & Townsend (52) was also examined by Cleverdon & Laker (59) who employed denitrated collodion membranes rather than polyvinyl alcohol membranes, and obtained quite different values for $\overline{M}_n$. Cleverdon, Laker & Smith (60) have suggested that these differences are real and depend on chemical differences between the membranes. In this connection, Flory (50) has suggested that discrepancies in values for $\overline{M}_n$ obtained in different solvents may be due to such factors as chemical degradation, association, or aggregation.

Rothman, Schwebel & Weissburg (61) have recently pointed out that it should not be assumed that sorption equilibrium between solution and osmotic membranes is quickly attained. These authors investigated the sorption of C^{14} labelled dextran on collodion membranes and found no equilibration even after seven days time.

Frank & Mark (62) report the measurement of osmotic pressure of four

polystyrene samples in benzene, toluene, and methyl ethyl ketone by a number of different laboratories. The data were fitted to a linear equation and it was found that the results from benzene and toluene solutions were in agreement, whereas those of methyl ethyl ketone solutions gave different values of both $\overline{M}_n$ and Γ_2. The results, on the whole, were badly scattered, which was thought to be a result principally of three factors associated with the properties of semipermeable membranes; (*a*) diffusion of solute through the membranes, (*b*) membrane dissymmetry, that is, structural peculiarities of the membranes, and (*c*) adsorption of solute on the membranes.

In conclusion, experimental uncertainties still obscure the precise description of osmotic pressure behavior of dilute high polymer solutions. It is evident that the chemical nature of the membrane influences the results, that the use of different membranes and solvents can lead to either curved or linear plots of π/c versus c, and that the magnitude of the effect of the third virial coefficient remains uncertain. Finally, while the most recent and complete theoretical treatment of osmotic pressure, that of Flory and Krigbaum, appears to fit, at least qualitatively, much of the available experimental data, it is evident that the further evaluation and development of osmotic pressure theory will require improved laboratory data.

Sedimentation and Diffusion

Sedimentation and diffusion are considered together since both are directly related to molecular mobilities, and since a knowledge of the two permits one to calculate molecular weights by use of Svedberg's equation:

$$M = RTs_0/D_0(1 - \overline{V}\rho). \qquad \text{XIX}$$

In this equation, s_0 and D_0 are the sedimentation and diffusion coefficients at infinite dilution, M the molecular weight, V the partial specific volume of the polymer, and ρ the solution density.

Recent determinations of molecular weights of high polymeric substances using sedimentation and diffusion methods include the following: Creeth (63) obtained a maximum molecular weight of 36,000 for crystalline insulin in solutions of pH around 7.4. This is in agreement with x-ray studies reported by Crowfoot (64) and with some earlier sedimentation data, but not with light-scattering results reported by Doty, Gellert & Rabinovitch (65), who obtained lower values but at a lower pH. These discrepancies appear to be a result of dissociation equilibria exhibited by insulin in solution. A basic unit of molecular weight equal to 12,000 appears to exist at low pH. These units tend to form dimers, trimers, and possibly tetramers as the pH is raised. Doty, Gelbert and Rabinovitch have formulated a theory of this type to explain their light-scattering data. Koenig & Perrings (66) have observed that the molecular weights of sodium desoxyribonucleate obtained from sedimentation data were much less than those obtained by light-scattering. It was suggested that these results can be explained by assuming

that light-scattering, a static method, measures large aggregates that are easily broken up in a centrifugal field.

Fessler & Ogston (67) prepared a polysarcosine polymer by Leuch's synthesis, and examined it by measuring sedimentation and diffusion, intrinsic viscosities and end-groups. Molecular weights calculated from end-groups were in substantial agreement with those calculated from s_0 and D_0.

There exists a considerable degree of interest in the dependence of sedimentation and diffusion upon concentration and molecular weight. Newman & Eirich (68) have summarized equations for the effect of concentration.

$$s = s_0(1 + K_s c)^{-1} \qquad \text{XX}$$

$$D = D_0(1 + K_d c). \qquad \text{XXI}$$

These equations assume a linear dependence of $1/s$ and D on c but if nonlinearity is observed additional power terms in c are required.

Golden (69) has recently discussed the concentration effect during sedimentation, taking cognizance of the fact that the concentration decreases during an experiment. Allowing for that effect, he obtained an equation for s_0. Golden also related sedimentation to intrinsic viscosity to obtain equations for the calculation of molecular weights from sedimentation rates and specific volumes alone.

Although the variation of the sedimentation coefficient with concentration is frequently found to obey equation XX—for example, in Fessler & Ogston's investigation of polysarcosine (67)—in other cases a more elaborate equation is required. Thus, Newman, Loeb & Conrad (16) fitted their sedimentation data for ethyl acetate solutions of nitrocellulose to quadratic forms and Scholtan (70) found the sedimentation constant of polyvinylpyrrolidone to be a linear function of $c^{1/2}$.

A linear dependence of diffusion coefficients on concentration has been observed by Newman, Loeb & Conrad (16) for nitrocellulose in acetone, by Tsvetkov, Kroser & Terent'eva (71) for polyisobutylene in hexane, and by Scholtan (70) for polyvinylpyrrolidone in water. On the other hand, Fessler & Ogston (67) observed nonlinear dependence in their studies on polysarcosine.

It is common to analyze the dependence of s_0 and D_0 on molecular weight by fitting straight lines to log-log plots. Most frequently, $1/s_0$ and D_0 appear to be proportional to M^a with a assuming values in the neighborhood of -0.5. Thus, Fessler & Ogston (67), in their study of polysarcosine, found that D_0 was proportional to $M^{-0.6}$ and consequently s_0 proportional to $M^{0.4}$. Scholtan (70) found that both $1/s_0$ and D_0 were proportional $M^{-0.5}$ for polyvinylpyrrolidone, Schulz & Meyerhoff (58) found s_0 proportional to $M^{0.43}$ and therefore D_0 proportional to $M^{-0.57}$ in the case of polymethylmethacrylates in chloroform. Mandelkern *et al.* (72) found s_0 for polyisobutylene in cyclohexane proportional to $M^{0.42}$.

Claesson, Gehm, & Kern (73) attempted to prepare a rod-like polymer and thought that a methyl-substituted polyphenylene prepared by the

Ullmann reaction between 4,4′-diiodo, 3,3′-dimethyldiphenyl and copper would be a polymer of this type. However, the measured sedimentation and diffusion coefficients were found to be proportional to $M^{0.5}$, which suggests a random coil structure.

Although most flexible polymers exhibit a relatively simple dependence of diffusion coefficient on molecular weight, Adelstein & Winkler (74) reported that D_0 of polystyrene in methyl ethyl ketone first decreases, then increases, with increasing molecular weight. This study has been extended by Luner & Winkler (75) to polyisobutylene in *n*-heptane, carbon tetrachloride, and benzene. The normal inverse dependence of D_0 on molecular weight was observed in carbon tetrachloride and benzene but not in *n*-heptane, where the unusual behavior noted for polystyrene in methyl ethyl ketone was observed. In contrast to the results obtained with polystyrene, these authors conclude that *n*-heptane is a poorer solvent than benzene for polyisobutylene, a conclusion at variance with viscosity results reported by Fox & Flory (76).

The quantities K_d and K_s, which appear in equations XX and XXI, have also been observed to be molecular weight dependent. Thus, Newman, Loeb & Conrad (16) found for nitrocellulose in ethyl acetate that K_s is equal to $0.015M^{0.50}$. Because of the exponent, K_s was accordingly considered proportional to the mean end-to-end distance of the nitrocellulose chains. Newman & Eirich (68) observed K_s to be proportional to $M^{0.5}$ for solutions of polystyrene in chloroform, toluene, and methyl ethyl ketone; and Tsvetkov, Kroser, & Terent'eva (71), in studying the diffusion of polyisobutylene in hexane, noticed that K_d was dependent on molecular weight and related to the osmotic pressure second virial coefficient.

Newman & Eirich (68) also related K_d to the osmotic pressure second virial coefficient and solute molecular weight as follows:

$$K_d = (2\Gamma_2 - K_s) \qquad \text{XXII}$$

Schulz & Meyerhoff (58) related the parameters K_s and K_d to Γ_2 by a similar equation and, as noted earlier, investigated the dependence on molecular weight of sedimentation and diffusion of polymethylmethacrylates.

Several recent papers have been concerned with the application of sedimentation and diffusion data to the determination of molecular dimensions. Thus, Koenig & Perrings (66) were able to calculate by combining sedimentation and viscosity data the dimensions of sodium desoxyribonucleate, assuming a prolate ellipsoid structure. Scholtan (70) has concluded that polyvinylpyrrolidone exists in solution as random coils containing immobilized solvent. This conclusion is supported by a correlated light-scattering investigation by Hengstenberg & Schuch (77). A calculation of root mean square distances between the ends of the polymer chains indicated that the chains of this polymer are tightly coiled in solution.

Miller & Hamm (78) have also studied the properties of polyvinylpyrrolidone, using sedimentation, diffusion, and viscosity data. When molecular

dimensions were calculated, assuming an ellipsoid model, an axial ratio in the range of 10–25 was obtained. In agreement with Scholtan and Hengstenberg & Schuch, they also concluded that polyvinylpyrrolidone is a hydrated coiled polymer.

Ogston & Woods (79) used sedimentation data to examine the molecular configuration of dextran, following the report of Ingelman & Halling (80) that dextran particles are quite elongated with an axial ratio between 17 and 100. Using procedures described by Fessler & Ogston (67) and by Ogston & Stanier (81), which permit the calculation of both the degree of asymmetry and of solvation, Ogston and Woods came to a different conclusion, namely, that dextran is not elongated, and that its axial ratio is less than 10 and may be close to 1. Their calculations also indicate that dextran is highly solvated.

Several new experimental procedures for obtaining diffusion constants have been reported. Free boundary methods, in which the boundary is observed by means of a split light beam have been described by Tsvetkov (82) and by Saini & Moraglio (83). They report that their method gives values of D good to ± 1 per cent. Other basically different experimental methods have also been described. These include diffusion from porous frits, reported by Wall, Grieger & Childers (84) and Wall & Childers (85), as well as diffusion in porous frits submerged under mercury, reported by Mysels & Stigter (86).

In connection with new theoretical treatments of sedimentation and diffusion, several recent papers should be mentioned. Peterlin (87) has derived expressions for semirigid macromolecules such as cellulose derivatives. Using for a model a linear molecule consisting of short links, he calculated the dependence of s on M and obtained an equation which permits the calculation of molecular dimensions. A relationship between s and molecular flexibility and hydrodynamic interaction was obtained. These equations were applied to experimental results obtained for nitrocellulose and cellulose acetate in acetone, methyl cellulose in water, cellulose in cuprammonium hydroxide, and polystyrene and chloroprene in chloroform, with results in agreement with general opinion regarding size and flexibility of these polymer molecules.

Mandelkern & Flory (88, 89) have developed equations for both diffusion and sedimentation which relate these effects to the theories of viscosity and osmotic pressure developed by Flory and co-workers referred to earlier. Mandelkern and Flory used an equation of Onsager & Fuoss (90) to relate the diffusion coefficient to the osmotic pressure virial coefficients as follows:

$$D/D_0 = [1 + 2\Gamma_2 c + (15/8)\Gamma_2^2 c^2]/(1 + k_1 c) \qquad \text{XXIII}$$

where the factor $(1+k_1c)$ expresses the dependence of the frictional coefficient on concentration. Equation XXIII indicates that D does not vary linearly with concentration.

Mandelkern & Flory (89) have also derived equations for the frictional coefficient analogous to those for viscosity and in so doing obtained an

equation relating the sedimentation constant to intrinsic viscosity:

$$s_0[\eta]^{1/3}/M^{2/3} = N^{-1}\Phi^{1/3}P^{-1}(1 - \overline{V}\rho)/\eta_0. \qquad \text{XXIV}$$

In the above equation P is a "universal constant" analogous to Φ of the viscosity theory, η_0 is the viscosity of the solvent, and $\overline{V}$ is the partial specific volume of the solute. To test this equation, measurements of s_0 and $[\eta]$ in the same solvent over a wide range of molecular weights are required. Mandelkern and Flory took data from the literature which confirmed the prediction that P is constant and derived a value of $\Phi^{1/3}P^{-1} = 2.55 \pm 0.20 \times 10^6$.

The diffusion coefficient was also related to viscosity as follows:

$$D_0\eta_0(M[\eta])^{1/3} = kTP^{-1}\Phi^{1/3} \qquad \text{XXV}$$

where k is Boltzmann's constant and T is the absolute temperature. Support for this equation was obtained from experimental data of Vallet (91) on the diffusion of polystyrene. These equations were investigated in more detail by Mandelkern *et al.* (72) using an experimental examination of the sedimentation of polyisobutylene in cyclohexane, a "good" solvent. These data also yield a value of $\Phi^{1/3}P^{-1} = 2.5 \times 10^6$. These authors also note that the correlation of sedimentation constants and intrinsic viscosities obtained by means of equation XXIV is more consistent than correlations obtained by means of equations derived from the Kirkwood-Risemann or Debye-Bueche theories for viscosity. These results are used as support for the Flory-Fox viscosity theory, out of which it is concluded that the root mean square end-to-end distance increases more rapidly than $M^{1/2}$. It is noted that an advantage of equation XXIV is that the molecular weight can be calculated from sedimentation constants in combination with intrinsic viscosities rather than diffusion coefficients.

Light-Scattering

The subject of light-scattering by solutions of macromolecules has been effectively reviewed by a number of authors including Zimm, Stein, & Doty (92), Mark (93), Oster (94), and Doty & Edsell (95). Very briefly, the theoretical basis of light-scattering can be summarized as follows:

For molecules of dimensions much smaller than the wave-length, λ_0, of the incident light, the molecular weight is obtained by the equation:

$$Hc/\tau = 1/M + 2Bc = \frac{1}{M}\{1 + 2RT\Gamma_2 c\} \qquad \text{XXVI}$$

where τ is the turbidity, c the concentration of polymer in solution, M the molecular weight of the polymer, and B the second osmotic virial coefficient. The quantity H is equal to $[32\pi^3 n_0^2(n - n_0/c)^2]/(3N_0\lambda_0^4)$, where n and n_0 are the refractive indices of solute and solvent respectively, and N_0 is Avogadro's number. Molecular weights are obtained by extrapolation of a plot of Hc/τ versus c to infinite dilution.

Alternatively, equation XXVI can be expressed in the form:

$$Kc/R_{90} = 1/M + 2Bc. \qquad \text{XXVII}$$

In this expression R_{90} is equal to $i_{90}r^2/I_0$, where i_{90} is the 90 degree scattered light intensity at distance r from the scattering molecules, and I_0 is the intensity of incident light. K is equal to $3H/16\pi$.

Many macromolecules, however, have dimensions comparable to the wave length of the incident light, thus giving rise to interference effects for scattering in other than the forward direction. This results in an unsymmetrical scattering which can be characterized by a dissymmetry coefficient, z, equal to i_{45}/i_{135}.

For large molecules equation XXVII can be rewritten as

$$Kc\ P(90)/R_{90} = 1/M + 2BP(90)c \qquad \text{XXVIII}$$

when $P(90)$ is a scattering function for 90°. It has been shown that these scattering functions are related to the dimensions of the solute molecules, viz:

$$\text{Spheres: } P(\theta) = \left[\frac{3}{x^3}(\sin x - x\cos x)\right]^2, \qquad x = sD/2 \qquad \text{XXIXa}$$

$$\text{Rods: } P(\theta) = \frac{1}{x}\int_0^{2x}\frac{\sin w}{w}\,dw - \left(\frac{\sin x}{x}\right)^2, \qquad x = sL/2 \qquad \text{XXIXb}$$

$$\text{Coils: } P(\theta) = \frac{2}{x^2}\{e^{-x} - (1-x)\}, \qquad x = s^2R^2/6 \qquad \text{XXIXc}$$

where s is equal to $(4\pi \sin \theta/2)/\lambda$, D is the sphere diameter, L the rod length, and R the root mean square end-to-end coil distance. It will be seen that as the molecular dimensions decrease, or as the wave length of light becomes infinite, the scattering functions approach unity, thus reducing equation XXVIII to equation XXVII.

Zimm (96) has developed an alternative method for treating light-scattering data to obtain M and B. This consists of plotting Kc/R_θ versus $\sin^2 \theta/2 + kc$, where k is a conveniently chosen constant. By a double extrapolation from a grid of points to $\theta = 0$ and $c = 0$, accurate values of M and B are obtained.

In a series of papers, Porod (97) and Kratky & Porod (98) have developed new scattering functions to fit the transition region between random coils and rigid rods. Porod points out that Debye's scattering function for a random flight coil as given by equation XXIXc fails to give the correct asymptotic value for a rigid rod. The model chosen in the most recent paper is that of rigid rods (vectors) linked together in such a way that the direction of the initial vector is propagated to some extent as a "persistent length." The earlier treatment of this model used a simplified concept of a continuous flexible thread so that integrations could be substituted for summations.

In his most recent paper, Porod introduces a length distribution function, $H_n(r)$. Since it appears that the scattering function is not too dependent on this distribution function (99, 100), Porod does not attempt to describe it completely but restricts the problem to determining the width of the distribution curves by calculating the averages, $\langle r_n^2 \rangle_{av.}$ and $\langle r_n^4 \rangle_{av.}$ To illustrate his

results, Porod calculates a function, δ_n, which is a measure of the width of the distribution curves, and also derives a scattering function of the form:

$$I = n + 2\sum_{m=1}^{n-1} (n - m)\{\delta_m \exp[-s^2\overline{r_m^2}/6] + (1 - \delta_m)\cdot(\sin s\tilde{r_m}/s\tilde{r_m})\} \qquad \text{XXX}$$

where m is a standard deviation. Plots of I, Is, and Is^2 versus s were made to show the transition point from which the "persistent length" is calculated. This scattering equation fulfills the requirement of describing continuously the transition from a random coil to a rigid rod.

Recent experimental determinations of size and shape include the following: Schulz, Cantow & Meyerhoff (101) used light-scattering and viscosity measurements for an experimental investigation of the dependence of the random-coil diameter upon molecular weight. Coil diameters of a series of polymethylmethacrylate fractions were calculated using light-scattering measurements and intrinsic viscosities. Molecular weights were obtained from sedimentation and diffusion coefficient determinations. When coiled diameters, d, were plotted logarithmically versus molecular weight, straight-line relationships were obtained indicating a dependence of the form: $d \sim M^{0.6}$, which departs significantly from the unrestricted random-flight prediction.

Bischoff & Desreux (102) also examined fractionated samples of polymethylmethacrylate by viscosity, osmotic pressure, and light-scattering measurements. Their results indicate that this polymer has a value for R more than three times the theoretical value for a random coil and that there is interaction between a polymer solute and a good solvent which affects the dimensions of the dissolved polymer molecules.

Light-scattering measurements have been used for determining the size and shape of sodium desoxyribonucleate. The molecular weight of this substance has been reported between 0.5 and 24×10^6 and its shape in solution has been described as a partially random coil (103), a rigid rod (104), an intermediate configuration with some branching (105), and a gel network (106). Rowen (107) has undertaken an exhaustive study of this molecule to resolve these discrepancies using light scattering, flow birefringence, viscosity measurements, and electron microscope pictures. The light-scattering results have been reported in full; from these studies, it is concluded that sodium desoxyribonucleate is a slightly flexible rod. In addition, the molecular length was shown to decrease as much as 40 per cent upon salt addition, indicating folding of the molecules. A molecular weight of 4.5×10^6 was calculated for their material. A preliminary report (108) of viscosities and electron microscope pictures indicates general agreement with the light-scattering results.

Peterlin (109) has likewise investigated the scattering of sodium desoxyribonucleate and has also concluded that the molecular configuration of this molecule lies between that of a random coil and that of a rigid rod. Peterlin characterizes the molecules in terms of the "persistent length," and notes

that while smaller molecules are more extended, the "persistent length" did not change with size.

Aggarwal & Long (110) have used light-scattering to examine the behavior of a terpolymer consisting of 37 mole per cent methylacrylate, 16 mole per cent dichlorostyrene and 47 mole per cent 2-vinylpyridine in neutral and acidic solvents. The mean-square length was found to be 650 Å in methyl ethyl ketone and to be 1180 Å in acetic acid. This increase in length is caused by the increased polymer charge resulting from interaction between acetic acid and polymer pyridinium ions. The viscosity behavior of this terpolymer in nitromethane demonstrates that this material is also capable of reacting as a polyelectrolyte with the *aci* form of nitromethane.

Bosworth *et al.* (111) have examined the dissymmetry of polyvinyl acetate in ethyl acetate. Coil diameters were calculated and it was found that the highest molecular weight fractions were relatively the least extended.

Doty, Schneider & Holtzer (24) examined the light-scattering and viscosity of cellulose derivatives (carboxymethyl cellulose and trinitrocellulose) to investigate the generally accepted concept that cellulose derivatives are more extended than vinyl polymers. These authors' viscosity results indicate that the end-to-end distances are approximately equal to one-half the contour length. Since these are non-Gaussian chains, it is suggested that dissymmetry measurements lead to too small dimensions if mean lengths are calculated. Doty, Schneider and Holtzer also state that the Flory-Fox equation does not apply to cellulose derivatives of low and moderate molecular weight, again because the chains are non-Gaussian. Φ was found to be of the order of 0.15×10^{21} instead of 2.1×10^{21}.

Paschall & Foster (112) have used 90° turbidity measurements to follow the breakdown and retrogradation of amylose aggregates under various experimental conditions. They showed that "native" aggregates of amylose break down slowly in 1 *N* potassium hydroxide and rapidly in neutral solutions. The turbidity of these neutral solutions subsequently rises, indicating retrogradation to a new type of aggregate sensitive to alkali degradation. Consequently, the investigation of the degradation of "native" aggregates is now simplified since alkali can be used to destroy retrograde aggregates.

The molecular weight of amylopectin, the branched chain component of starch, was measured by Witnauer, Senti & Stern (113). A value of 36 million was found for a potato amylopectin, compared to values previously reported ranging from 200,000 by end-group methods to 420 million (114) obtained by light-scattering from an acetylated product.

Frenkel (115) has measured the molecular weight of a number of proteins to obtain values varying from 17,500 for trypsin to 295,900 for edestrin. The effect of denaturation on molecular weight was also reported. Denaturation by heat caused a three-fold increase in the molecular weight of serum albumin. On the other hand, acid denaturation caused a lowering of the molecular weight of edestrin and chymotrypsin.

Several years ago, Ewart *et al.* (116) reported the effect of mixed solvents on slope and intercept of plots of Kc/R_{90} versus c. Apparently anomalous results were explained in terms of selective adsorption of the better solvent by the polymer, thus leading to a higher apparent molecular weight. A further theoretical treatment of this problem from a thermodynamic viewpoint has been published by Kawai (117), who derived a method for obtaining a quantitative estimate of the degree of adsorption of the better solvent on the polymer.

An experimental investigation of the turbidity of polystyrene solutions in mixed solvents is reported by de Brouckère & Anspach (118). After examination of mixtures of toluene with a variety of other organic solvents in light of the Kirkwood-Goldberg theory (119), these authors concluded that toluene was usually preferentially adsorbed on the polymer particles in solution. Exceptions included solvent mixtures containing cyclohexanone or dioxane. When these results were compared to the differences between the cohesive energy densities of toluene and precipitant, no correlation was found, indicating that cohesive energy densities are not a reliable index of solvent power for polystyrene. In another paper concerning light-scattering from multicomponent systems, Guinand, Labeyrie, & Tonnelot (120) considered the possibility of following protein reactions by means of light-scattering. The 90° scattering from solutions of mixtures of two proteins was examined with the conclusion that the scattering from such mixtures is meaningless unless the scattering diagram is rigorously symmetrical.

Blum & Morales (121), considering a solution containing z polymer components, have derived the following equation for such a solution:

$$\frac{kc}{I(\theta)} = \left[1 \Big/ \sum_{i=1}^{z} M_i P_i(\theta) x_i\right] + 2E\left[\langle\sqrt{A_2^{(ii)}}\rangle_{Av}\right]^2 c \qquad \text{XXXI}$$

where M_i are molecular weights, $P_i(\theta)$ are scattering functions, x_i are weight fractions of polymers 1 to z, c is the total concentration and $A_2^{(ii)}$ is an interaction factor. Equation XXXI is a generalization of equation XXVIII for light-scattering employed by Zimm.

Several recent papers have been concerned with experimental procedures. Measurements of the molecular weights of four standard samples of polystyrene were made in a number of different laboratories under the auspices of the International Union of Pure and Applied Chemistry (62). Light scattering results were found to be considerably more consistent than intrinsic viscosity or osmotic pressure measurements. This suggests that light-scattering is the most reliable experimental method among the three for obtaining molecular weights of polymers.

Bosworth *et al.* (111) have designed a new light-scattering instrument in which the incident beam is rotated by a mirror system while the photomultiplier tube is kept stationary. Better results are claimed for this instrument because electrical instability, due to moving the photomultiplier tube, is eliminated.

An improved differential refractometer has been described by Schulz, Bodmann, & Cantow (122). Compared to earlier instruments, it is reported that this instrument yields values good to one additional decimal place. Oster (123) has recommended a 3 per cent Ludox (colloidal silica) suspension in water as a standard for calibrating light-scattering equipment. This suspension has the advantages of being stable and readily available. It shows no dissymmetry at 4360 and 5460 Å, no depolarization, and its optical density is proportional to λ^{-4}. Finally, Brice, Nutting, & Halwer (124) describe methods for correcting for absorption and fluorescence for light-scattering molecular weight determinations involving colored or fluorescent materials.

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COLLOID CHEMISTRY[1,2]

EXCLUSIVE OF HIGH POLYMERS

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This review will be restricted to the lyophobic colloids where, in most cases, the stability is believed to be due to the presence of an electrical double layer; but where, at the same time, the particles may be considered as rigid. That is to say, the dimensions of the kinetic units are, apart from aggregation, by no means related to their charge density, as contrasted with the polyelectrolytes where the extension and shape of the units may be influenced by their electrical state to such an extent that often the expression "particle" becomes meaningless.

Thus, in studying lyophobic colloids the particles are treated as a "wall" in equilibrium with the liquid, the preferent and spontaneous adsorption of one species of ions giving rise to the formation of the double layer.

Reviews.—A general survey of the progress of the study of lyophobic colloids may be obtained from *Colloid Science I*, an extensive treatise on hydrophobic colloids by Kruyt, Overbeek & Jonker (1a). Stress is laid upon the fundamentally irreversible character of lyophobic systems. Besides the chapters on phenomenology, optics, and on rheology, the book contains a detailed study of the electrochemistry of the double layer and of the electrokinetic phenomena. The well-known theory of the stability of these systems by Verwey & Overbeek (1b) is treated in a comprehensive way by the latter. The outline of this theory has already been accepted by many investigators and, in several aspects, has been completed by others. However, some authors have questioned the role of the attraction forces which are thought to oppose the electrical repulsion forces in governing the stability, and have attempted to give an alternative concept. We may state in advance that a comparison of computed coagulation values with those found experimentally, has so far failed to provide a quantitative proof as too many factors are joined into the theoretical results. The merits and weaknesses of one or another treatment might rather be demonstrated by investigating repulsion and attraction forces separately. Moreover, it will be wise to take into account the multiplicity of facts, thus considering not only coagulation phenomena but the phenomena revealed by investigation into electrokinetics and electrode processes as well.

[1] The survey of the literature pertaining to this review was concluded in November, 1953.

[2] In the preparation of this summary the author has had valuable discussions with Mr. Th. Payens, Mr. H. Koelmans, and Mr. H. Sparnaay and wishes to express his thanks for their helpful assistance.

Duclaux (2) wrote an introduction to colloid chemistry without differentiating between lyophilic and lyophobic systems, thereby neglecting the irreversibility of the latter. Booth (3), in a review which is both historical and critical, gives an elucidation of the theory of the double layer, and a discussion of the results obtained upon its application. This paper, therefore, covers a most important part of colloid chemistry; it points out very clearly the areas of investigation in which the theory fails to be productive, and weighs differing points of view with great objectivity.

Double Layer

Theory, structure.—The theory of the diffuse double layer was extended by Grahame (4) to the case of electrolytes of unsymmetrical valence type, restricting his treatment, however, to bivalent ions. The results can be summarized as follows: the integral or the differential capacity of the double layer no longer show the minimum value at the zero point of the potential, as a consequence of the different charge distribution on both sides of the zero point of charge. At the mercury interface this result could be verified experimentally for very dilute solutions of 2:1 and 1:2 electrolytes. Theoretically, it was shown that the variation of the double layer potential with the distance from the wall (as far as large distances are concerned) diverges less from the exponential law if the metal surface bears the same charge as the most abundant ion; (for example, if the mercury is both negatively charged and in contact with a $BaCl_2$-solution).

To exclude the high charge densities at the wall, to which application of the Gouy-Chapman theory leads, Freise (5) corrects, by a thermodynamic treatment, the Boltzmann theorem for the finite dimensions of the ions. In this way volume effects are taken into account over the whole range of the double layer and not exclusively in the first ionic layer near the wall as is done in the Stern theory. The volume ratio of ions and solvent molecules is essentially taken to be varying, though in view of mathematical difficulties a simple proportion ($\frac{1}{2}$, 1 or 2) is assumed. In this respect his results, as far as volume corrections are concerned differ from those arrived at by Bikerman who earlier, made a similar approach (6). He presents ψ-curves showing, in general, the usual shape, the steepest part near the wall now being slightly curved instead of straight.

Free energy.—Following an entirely statistical method, Ikeda (7), derived the expression for the free energy of the double layer near a charged surface, first obtained by Verwey & Overbeek (1b) who used a thermodynamic approach. The first method devised by the latter authors according to which the double layer is thought to be formed by step-wise charging up of the surface, was confirmed. Their second method, supposing a discharging of the ions present by transporting small quantities $ed\lambda$ to infinity, was confirmed too, with the restriction that a correction was needed if the surface was not flat. The partition function with which Ikeda starts, describes the

interaction of the ions with the wall and with each other. For curved surfaces a correction term is introduced indicating that if ψ_0 is to be constant, an electrostatic charge will be left on the surface when all ions have been discharged.

As long ago as 1950, Levine remarked that this correction should be present. Later on, Overbeek, in his treatment in *Colloid Science* (1a), included this term as an integration constant. Recently, Levine (8) in a discussion of the charging process of a single double layer and the interaction of two double layers in which a modified Poisson-Boltzmann equation was used, has calculated the corrections due to fluctuations of the potential in the solution, to dielectric saturation, to electrostriction and to the finite size of hydrated ions. These corrections proved to be of minor importance. At the same time, Williams (9) applied the Loeb-correction (10) to a single flat surface; this means that the self-atmosphere effect of an ion in the neighborhood of a colloidal particle has been considered.

Correlation.—Vasenin (11) investigated the possibility of calculating the zero point of charge of a metal placed in an electrolyte solution by relating the contact potentials of two different metals. This means that one neglects all possible potential shifts due to dipole orientation and to the rearrangement of the ionic charges of the liquid in the neighborhood of the wall. The contact potential can be substituted by the work-functions of the metals. Mathematically, one arrrives at the relation $\epsilon_2=\epsilon_1-b(\phi_1-\phi_2)$, where ϵ means the zero point of the potential of a metal relative to the normal hydrogen electrode, ϕ is the work function of the metal, and b a correction factor accounting for possible neglections.

Out of a graph of ϵ_2 and $(\phi_1-\phi_2)$ one gets a nearly straight line, from which the value of ϵ_1 can be deduced. The deviations from this behavior could be represented formally by a double layer potential $\psi=A$ exp. $(B\phi)-b\phi$, A and B being empirical constants taken from the plot of ϕ versus ϵ.

Experiments.—The influence of slightly soluble organic substances on the capacity of the dropping mercury electrode in alkaline and acid solutions was the subject of an investigation by Gupta (12). From this examination one concludes that the adsorption of substances like camphor, ether, and amylalcohol at the mercury surface is less dependent on the potential of the mercury surface than the adsorption of more apolar substances like benzene or toluene.

The friction shown by a spherical glass bearing supported by a metal surface with the point of contact surrounded by an electrolyte solution, is distinctly influenced by a potential difference set up between the metal and the solution, as was stated once more by Bockris & Parry-Jones (13). A close resemblance to the electrocapillary curve for the given system could be stated. The facts suggest that the maximum of friction, as measured by the rate of damping of a pendulum, can be identified with that of the electrocapillary curve, corresponding to the charge-free surface. Thus, the electric

repulsion between the glass and the metal diminishes the load. It may be added, that the potential difference proved to have no influence on the hardness.

The electrical properties of oil/water interfaces have been once again investigated by Karpfen & Randles (14). The electrical potentials occurring at such interfaces are attributed to the partition of ions between the oil and the water phase. By thermodynamic reasoning, phase boundary potentials are now related to the partition coefficients of both anions and cations. These partition coefficients were measured and the potentials computed from emf. measurements on a cell where special care had been taken to suppress the influence of liquid junction potentials. The experimental results agree fairly well with the theoretical predictions.

Measurements of Forces

As long range forces were introduced into the discussion of stability about twenty years ago, much attention should be paid to any effort that may yield experimental evidence of their existence or rather of their magnitude and range.

Direct measurements of the van der Waals-London forces have been undertaken by Overbeek & Sparnaay (15). The distance between two flat, highly polished glass or quartz plates and their parallelism could be estimated by observing the Newton interference colors. One of the plates was attached to a fairly stiff spring, the bending of which was measured with an accuracy of about 10 Å. At distances less than 6000 Å the establishment of the equilibrium is often difficult, very likely because of the presence of fragments of silicagel protruding from the surfaces.

Interpreting the results according to the formula $K = AO/6d^n$, where K is the force, O the surface area and d the distance of the plates, the exponent n proved to be 2.7; but a value of 3 may not be ruled out, as the experimental points are rather scattered. When $n = 3$, A is found to be 3.4×10^{-11}; this value is about 30 times the value expected (10^{-12}). A possible explanation may be given, supposing that the long-range forces are not strictly additive, i.e., that neighboring atoms account for a considerable increase in the attraction without violating the force-distance relation.

On the other hand, repulsion forces between two charged surfaces may be demonstrated by studying the disjoining pressure of thin polymolecular liquid films. Evans (16), repeating experiments of Derjaguin & Kussakov (17) and Elton (18), in which the dependence of the equilibrium thickness of a waterfilm between glass (or silica) and air on the air pressure was measured, was able to explain the serious discrepancy between the results obtained by the latter authors.

With extremely pure water the film thickness is of the order of some hundreds of Angstroms, as found by Elton. If, on the other hand, a slight amount of surface-active substance (i.e. Na-hexadecylsulphate) is present, the film is suppressed only to a thickness of about 1000 Å, otherwise behav-

ing in the manner of the films reported by Derjaguin and Kussakov. The attainment of the equilibrium is then very slow, the adsorption being retarded by the limited volume in the disjoining film. As a consequence, the higher surface tension of the film causes liquid to be sucked toward the center. For this reason a false equilibrium may be found.

Stability

Aqueous systems.—Flocculation measurements on aqueous solutions of silver chloride were performed by Amiot (19). Here, the light absorption is used as a tool. Electrolyte is added immediately after mixing solutions of silver nitrate (0.003 *N*) and of potassium chloride (0.006 *N*) and the transmitted light is then measured over a certain period. If, with S as the optical density, dS/dt is plotted against the concentration of the coagulating electrolyte at constant times, maxima are obtained, the position of which varies only slightly with time. The corresponding salt concentrations should represent characteristic coagulation values.

In the field of emulsions, mention should be made of an investigation by van den Tempel (20) on the stability of oil in water emulsions. When considering the coagulation of such emulsions, a distinction should be made between the two subsequent stages of the agglomeration process: (*a*) the flocculation, and (*b*) the coalescence of the flocculated oil drops. From measurements of the amount of soap ions adsorbed at the oil/water interface and of the electrophoretic velocity, the potential drop extending into the aqueous phase was found to be of the order of 100 mv. Such a potential would give rise to an extremely high potential energy barrier between the emulsion drops as a consequence of their large size. Moreover, crossing this high potential barrier would result in a practically irreversible flocculation as the distance between the flocculated drops will be of the order of 1 Å. One would expect, therefore, the coalescence to occur immediately after the flocculation. On the contrary, one finds experimentally that the coagulation is often of the reversible type.

Van den Tempel now suggests that the flocculation may occur in the so-called secondary minimum of the potential interaction energy curve. This secondary minimum is found theoretically at a distance from the wall where the repulsion energy is approaching zero, if the attraction energy still has a small negative value, as may often be the case. Until now it has proved to be a rather weak point in the theory of the stability of hydrophobic sols by Verwey and Overbeek. Experimental evidence is provided by the fact that in the sedimentation of stock emulsions a separation in two distinct layers occurs, with a sharp boundary always between them; the top layer only containing the smaller particles. Now, indeed the depth of the secondary minimum increases rapidly with increasing particle size.

Van den Tempel states that the influence of the valency of the counterions on the rate of coagulation follows the rule of Schulze-Hardy. This fact, however, does not decide the question whether the flocculation is of the

ordinary or of the secondary minimum type. In all cases the rate of flocculation was found to exceed the rate of *rapid* flocculation as predicted by the theory of Smoluchowski, which might possibly be explained by the large particle size and by the particle size distribution of the emulsion.

Cockbain & McRoberts (21) working on the same subject, paid attention primarily to the phenomenon of coalescence. They studied the coalescence of both oil and water drops at a plain oil/water interface, in the presence of various amphipatic substances. The greater lifetime of oil drops in water compared to the lifetime of waterdrops in oil stabilized with the same water-soluble detergent, as found experimentally, cannot readily be attributed to film characteristics such as viscosity or elasticity, since these quantities should be the same, whichever phase is the continuous one. Electric effects are supposed to be of minor importance too.

The authors correlate the degree of stability (to coalescence!) of emulsions to the wetting or non wetting of the surface film between the drops by the discontinuous phase. Partial removal of the protecting film by wetting through the continuous medium is hampered by steric hindrance. This approach readily explains why an oil-soluble detergent tends to stabilize a W/O emulsion and vice versa.

A trend of thought entirely divergent from that expressed in the papers on stability so far reported in this review, has been followed for a number of years by Težak and his co-workers (22). In the first place, the article quoted gives a review of the work done at the Yugo-Slavian school on silver halide sols. In contradistinction to many others, these workers prefer to investigate the phenomena of coagulation on sols in statu nascendi. Since they are not in equilibrium, these sols seem not to be the most suitable, and the curves given for the extinction in relation to the concentration of stabilizing or coagulating ions are very complicated, showing strong dependence upon time. It seems possible, however, to separate coagulation effects from those concerning nucleation and crystallization. Coagulation values are found showing the Schulze-Hardy rule mentioned previously.

In discussing the results, the authors decline to introduce long range forces as a cause of coagulation, since this would entail addition of a new vague factor. More or less following the work of Ostwald, coagulation is seen as resulting from the state of the electrolyte solution. To confirm this, a linear relation between the logarithm of the coagulation values and the critical distances as defined by Bjerrum is demonstrated. At electrolyte concentrations where the sols are becoming unstable the authors declare that the ions constituting the surface charge on one side show a strong tendency to form ion pairs, with the counter ions on the other side, thus giving rise to a suppression of the double layer. Instead of the attraction forces a rather obscure osmotic mechanism is introduced.

In a separate paper, Vouk (23) has tried to derive Ostwald's activity coefficients rule from a formula given by Verwey and Overbeek. In substituting the coagulation value of $V8O$ in the Debye-Hückel formula for the ac-

tivity coefficient, one obtains log $f_{coag} \approx$ const., for rather high values of the double layer potential. Although Ostwald's rule was never confirmed experimentally in a satisfying way, it nevertheless appears from Vouk's reasoning that a rule such as Ostwald's does agree comparably with the facts, the activity coefficient being strongly related to the thickness of the double layer.

Nonaqueous systems.—The derivation of stability conditions by consideration of the free energy of a system of parallel plates or of spheres, if a double layer is present, i.e., with ions accumulating on the wall of their own accord, has induced an analysis of how far stability may be gained by nonionic molecules that are adsorbed in an equally spontaneous manner.

First expressions for the adsorption isotherm and for the surface tension are given by Mackor & van der Waals (24), using the model of a localized monolayer and allowing for the interaction between the adsorbed molecules due to steric hindrance. The authors applied a statistical technique to the problem of two parallel adsorbing plates. If brought closer together, the free energy rises because of the interaction of the adsorbed layers. An expression for the repulsion energy is given. For certain dispersions, as is stated explicitly, this effect must be responsible for the stabilization. Evidently, a stabilization mechanism as has been pictured in this treatment will be of interest, especially in the case of suspensions in apolar liquids, where electrolytical dissociation, if any, will be extremely small, and where the formation of a double layer, able to stabilize, is therefore said to be very unlikely.

It may be stated in advance, however, that a different explanation has been given by van der Minne (55) as a result of his experiments on electrophoresis in nonpolar liquids. Therefore, it may be reported more suitably in the section dealing with electrokinetics. Moreover, an objection may be raised to the theory of Mackor & van der Waals: a rather deep, secondary minimum is to be expected as the repulsion starts here very abruptly, i.e., at a distance equal to the length of the adsorbed molecule. So, at best this theory accounts for the stability of the finest particles in a suspension, e.g., of soot.

The settling of carbon black in a number of organic liquids has been studied by Garner, Mohtadi & Nutt (25). To give an explanation of the experimental results obtained with unstable systems (i.e., to account for the rate of shrinking of a coagulum) an outline is given of a theory in which the suspension is supposed to build up quite a loose chain-scaffolding structure already in the first stages of the aggregation. Gradually, the enmeshed particles, at first still free, will coagulate on this network, causing it to collapse from overweight, while a sharp boundary between the suspension and the supernatant liquid is maintained. Factors determining the rate of shrinking are, according to this theory: (a) the diffusion constant of the particles, (*b*) the density and the volume of the expelled liquid, and (*c*) the interfacial tension at the particle surface.

Some stable systems are described, e.g., with detergents or in nitrobenzene or aniline, where particles are moving free, forming a dense sediment only after weeks or months.

Suspension Effect

There has been much discussion (26) about the interpretation of potential measurements in colloid systems, in which many more difficulties are encountered than in simple ionic systems.

Especially in the use of salt bridges, different emf.'s are found depending on whether the liquid junction is made in the suspension itself or in the equilibrium liquid. In the first case the concentration of the suspension is an influential factor. It is already known from the work of Rabinovitch & Kargin (27), of Du Rietz (28) and of Loosjes (29), and as has been stressed by Sollner (30), that a reversible electrode can never be held responsible for these effects which are often called suspension effect and solconcentration effect. The difference arises at the place of contact with the salt bridge, a boundary which is decidedly in a state of nonequilibrium. Furthermore, the suspension effect can be shown to be identical with the Donnan emf., which may be defined as the emf. of the cell obtained by connecting one of two identical electrodes by means of a saturated salt bridge to a suspension and the other to its equilibrium liquid, both being in contact.

Recently, Overbeek (31) pointed out that a separation of this emf. into two liquid junction potentials and a membrane or "true" Donnan potential is quite abitrary, and that one is at a loss to know what assumptions must be made about the ion activities. On the other hand, by treating the Donnan cell as a sum of three liquid junction potentials all arbitrariness can be avoided.

Electrokinetics

Theory.—As far as the theory of the electrokinetic phenomena is concerned, a very important step forward was made, when the thermodynamics of irreversible processes were first introduced into this field by Mazur. Before this, in using a model, e.g., for a diaphragm, relations between the different electrokinetic phenomena could be derived, but the suitability of some model or other still remained dubious. Now, in applying nonequilibrium thermodynamics, all relations can be derived without any assumption about the structure of the diaphragm, regardless of surface conductance. The electrokinetic effects should be only linearly dependent on the generating pressure or current; a condition which will be fulfilled if these quantities are kept small. Electroosmosis and streaming-potential were treated by Mazur & Overbeek (32), more recently by Overbeek (33), and sedimentation potential and electrophoresis by de Groot, Mazur & Overbeek (34). It appears that only three independent constants govern the electrokinetic phenomena. Two of them are related to the electrical and hydrodynamic resistance, respectively, and the third one is closely related to double layer properties,

The choice between the experiments should thus be governed by convenience and not by principle. Again, it is true, the interpretation of the experiments in terms of ζ can only be reached by analysis of a model.

In further examination of the dependence of the electrokinetic effects in a diaphragm on its properties, Overbeek & van Est (35, 36) considered a net work of capillaries as a model. Putting E/P (streaming-potential) $=-V/I$(electroosmosis) $=ZRC$, where R is the actual resistance and C the capacity of conductance of the network, the authors showed that Z may be identified with $\epsilon\zeta/4\pi\eta$, when the surface conductance of the network is negligible or when all capillaries have equal cross sections. If these conditions are not fulfilled, it is not possible to make a general statement, as the value of Z depends on the detailed structure of the network. Still it may be said that a value of Z larger than $\epsilon\zeta/4\pi\eta$ will be rather exceptional, whereas, a lowering of Z is often to be expected.

At the same time networks of diaphragms were studied by Lorenz (37), who derived expressions similar to that of Overbeek & van Est. Such considerations are of practical interest, as often diaphragms are connected in parallel or in series, e.g., when enclosing a powdered material between two plugs of another material. Lorenz (38) also brought forward experimental evidence in this field, in measuring streaming potential, streaming current, and electroosmotic counter pressure on quartz in acetone, the quartz being held between two perforated platinum discs.

Aqueous systems.—Years ago Rutgers (39) introduced the measurement of centrifugation potentials as an alternative method in determining ζ-potentials. This method has been applied on the As_2S_3 sol and recently on the AgI sol (40). On adding indifferent electrolyte (i.e., potassium-nitrate) to these sols a decrease of ζ, followed by a slow rise is found. The minimum occurs at about 3 mM KNO_3. However, in computing ζ values, the authors have used a formula in which the presence of a relaxation effect, inevitably following from the treatment by irreversible thermodynamics, has not been taken into consideration.

In many respects related to the foregoing, is an approach to the determination of the electrokinetic charge which was given some years ago by Elton (41). When the sedimentation velocity of particles is measured in a given solution and in a concentrated salt solution, the density of electrokinetic charge is calculated according to the formula:

$$\sigma^2 = gx(u_0 - u)(\rho_2 - \rho_1)/MA_0^2 u\, u_0\rho_2$$

using u and u_0 as the two sedimentation velocities, ρ_2 and ρ_1 the densities of the particle and the liquid, respectively, M the total mass of particles per cc., A_0 the surface area/gr. and x the specific conductivity of the suspension.

From this the ζ-potential is evaluated using a formula of Verwey and Overbeek. Particles have to be as uniform as possible. The method was then applied (42a, b, c, d) to suspensions of quartz in conductivity water and in aqueous solutions of chlorides and nitrates. Both anions give nearly the

same results if combined with monovalent cations, but the nitrates of divalent cations show higher charge densities than the corresponding chlorides. Particle interaction may be ruled out, as the result is independent of the particle dimensions and of the concentration of the suspension in the investigated range. The experiments with purest water showed clearly the potential-determining influence of the hydrocarbonate ion.

Quite a different technique is required when streaming potentials are measured using an alternating (sinusoidal) pressure. Packard (43) deriving an equation along classical lines but neglecting the surface conductance and the diffuse ion distribution of the double layer, found a good agreement with the results from measurements carried on with glass capillaries in a frequency-range from 20 to 200 c.p.s. and for pressure amplitudes up to 20,000 dynes/cm.^{2}

The so-called electroosmotic phenomena reported by Laszló (44) studied by applying an A.C. voltage to two different liquids chosen from water, alcohols, ketones, etc., and separated by a filter glass plate, seem to bear little relationship to the true electrokinetic phenomena studied on walls in equilibrium with homogeneous liquids.

To explain the appearance of streaming potential and electroosmosis a mechanism, different from the classical has been proposed by Rose & Moss (45) and by Nash & Lister (46). According to these authors, the application of a pressure difference to the terminals of a capillary (or of a porous plug), would produce a dislocation of the diffuse charge along the whole length of the diaphragm. It may be mentioned, however, that an extremely small number of displaced ions may cause a potential difference, by which further transport of electricity will be avoided. To what extent the classical treatment is "defective" is not made clear.

Davies (47) investigated the electrophoresis of silver bromide sols. On addition of Ag ions, reproducible results could not be obtained unless AgF instead of $AgNO_3$ solutions were used. Presumably, silicate complexes originating from the glass and attaching themselves to the AgBr particles are removed by the F ions, forming fluorosilicate ions which are not adsorbed.

Hazel & Schnable (48) studied the ζ-potentials computed from streaming-potential measurements on "phosphors" and glass in solutions containing potassium silicate or barium acetate or both reagents together. Just as was found earlier in using solutions of sodium sulphate instead of barium acetate, here, too, the reduction of ζ of both phosphor and glass to a certain low value (ca. 40 mv.) involves an excellent adhesion of the phosphor particles to the glass, as is required in settling television screens. The action is explained in the following way: when close contact between the sedimented particles and the glass has been accomplished by lowering the repulsion force, the polymerization of the silicate adsorbed on the particle begins, inducing adhesion in all areas of contact.

This polymerization would occur preferentially at the solid surfaces, since the silicate is concentrated there by adsorption. There is evidence that

negative charges on the silicate skeleton play a role in bond formation, and it is suggested that hydrogen bonds are involved.

In this connection some investigations concerning the polymerization of silicic acid may be mentioned. Hurd *et al.* (49) are drawing attention to some observations showing the gel formation to be reversible. Prolonged dialysis causes the silicic acid gel to be completely hydrolyzed.

Brady, Brown & Huff (50), using light-scattering technique and viscosimetry looked into the gelation of potassium silicate solutions, focusing attention upon the influence of both the salt concentration and the pH. The rate of the salt-induced polymerization proved to be proportional to the fourth power of the salt concentration. The dependence on temperature pointed to a minimum of activation energy at pH $\sim$8. The following remarkable fact is reported: if an acid-induced polymerization is stopped by adding alkali and salt together a breakdown occurs, followed by a renewed polymerization. From this it would follow that the bonds formed in the first polymerization are different from those formed in the latter.

Nonaqueous systems.—Attention has already been directed to the opinion (51), that in liquids with a low dielectric constant, especially lower than 5 as in the hydrocarbons, particles can not build up a double layer nor show any electrokinetic phenomena worth mentioning, since ions are practically absent. Obviously, the investigations of LaMer & Downes (52), of Fuoss (53), and of Kraus (54) which made clear that ions can exist even in solutions of hydrocarbons, have been neglected. As a matter of course, the chemical character of the electrolytes dissociating in these solvents has to meet some requirements: one or both ions must have a good "solubility" in the solvent; in this case the interaction forces together with thermal motion easily overcome the interionic electrostatic forces. The absolute amount of ions is still very low.

Van der Minne & Hermanie (55) were able to state that suspensions of carbon black, rutile, lead chloride, or water as well as suspensions of aluminium or antimony show perfect electrophoresis when all suspensions are prepared in s solution of calcium diisopropylsalicylate (Ca-dips) in benzene. All suspensions were positive, the electrophoretic velocity being 0.1–0.3 μ cm./V sec. and the field strength 100 to 200 V/cm. One will note that the particles in the suspensions mentioned first have a high dielectric constant, in the latter, a high conductance.

Adding an oxidation resin instead of the Ca-dips to the benzene caused the suspensions to be negative. Reliable results could be obtained only after the construction of a new electrophoresis cell, increasing the resistance of the cell walls by diminishing the thickness of the glass or quartz wall, eliminating the surface conductance by treating the walls with silicones and by applying a vacuum jacket. All these precautions are not necessary, however, as soon as the conductivity of the liquid in the cell exceeds 10^{-10} or 10^{-9} mho. cm.$^{-1}$. Polarization phenomena are avoided by applying a relatively low field strength as indicated, since an upper limit is established by the

nature of the suspended material. The form of the particles is of main importance, as could be shown by comparing Al particles in globular form and in the form of leaflets. Moreover, at very low electrolyte concentrations there appears a "running-in" effect, probably due to a charging of the small capacitor formed by the cell. With the construction of this electrophoresis cell, we may state that the uncertainty about the value of results (as often reported) which are obtained in ordinary cells or by the use of high voltages, has come to an end; obviously these results are quite meaningless.

Van der Minne and Hermanie studied the correlation between flocculation phenomena and the electrophoretic behavior of different suspensions of carbon black with Ca-dips or tetraisoamylammonium picrate (Tiap), or mixtures of these reagents in benzene solutions.

In general, suspensions showing an electrophoretic velocity larger than a critical value (0.07–0.08 μ cm./V sec.) are peptized; those showing a smaller value are flocculated. From this a critical ζ-potential is then found to be 21 to 24 mv. In aqueous suspensions a distinct critical value is often postulated but not found, at least not for univalent ions.

Proceeding with adsorption measurements, the authors were able to demonstrate that a close correlation exists between adsorption and electrophoresis, the excess of one reagent or another on the surface of the particles determining the sign of the ζ-potential. No electrophoresis occurs unless a sufficient number of ions is present in the solution; therefore, at very low concentrations where the adsorption is 100 per cent, the particles do not move.

It will be clear that, according to van der Minne, the concept of an electrical double layer may be equally useful in the case of apolar media. So, the stabilization mechanism, proposed by Mackor & van der Waals and reported above might be superfluous; moreover, experimental evidence supporting their view is rather poor [see van der Waarden (56)].

In these systems it may be stressed, flocculation, upon the addition of electrolyte will be effected, not by a reduction of the double layer thickness (the ional concentration is far too low), but by partially superseding the adsorbed ions by others of the opposite sign. Regarding the influence of the dielectric constant, the experiments show clearly that "Coehn's rule" (57) is without foundation.

Dielectric Constant

It seems attractive to use the dielectric constant of disperse systems as opposed to optical measurements in characterizing their state, especially because concentrated systems may be used. As suggested by Voet (58), the dielectric constant may be measured as a function of concentration and of shear, using a cylindrical capacitor cell, one of the electrodes of which can be rotated.

Now dielectric constant and dielectric losses provide information only

about the form of the suspended particles, not about their dimensions. That indeed, is applicable also for conducting particles ($\epsilon = \infty$). Nor is aggregation demonstrated unless it affects the form factor as may be seen from the formula $\epsilon_S = \epsilon_0(1+3\ fV)$, ϵ_S being the dielectric constant of the system, ϵ_0 that of the medium, V the concentration by volume and f the form factor. In systems where the dielectric constant of the particles and of the liquid are comparable, a form factor is not perceptible. In such cases, measurements of other properties, e.g., the electrical conductance on shearing, may be indicated.

By Bondi & Penther (59, 60) suspensions of soap fibers and of silica particles in oils were chosen as nonconducting systems, the first containing quite anisometric crystalline particles, the latter amorphous and isometric ones. Rather unexpected is the extremely rapid response of the dielectric properties to both an increasing and decreasing rate of shear. It is supposed that an elastic deformation of structural elements (gel lumps) occurs in the sheared system. On shearing the suspensions with nonconducting particles the two cylinders show an "electrokinetic" potential difference of some hundreds of mv's, an effect that is left unexplained.

Systems containing conducting particles were represented by suspensions of iron powder and of carbon black in oil.

If we may generalize upon the results obtained in measuring the dielectric constant or the conductivity, we may conclude that shearing forces cause a deflocculation, tearing aggregates apart and producing, at the same time, an agglomeration or catenation, pressing particles together. Depending on the stability of the given system, one of the two effects will dominate, the shearing stress determining the size and shape of the equilibrium aggregate. In respect to the effect of shear, a study by Manley & Mason (61) on the collisions of uniform spheres in sheared suspensions may be mentioned also.

Viscosity

Electroviscous effect.—In adding electrolyte to an aged sol of silver iodide, Harmsen, van Schooten & Overbeek (62) found a decrease in viscosity. At the same time, there was a marked influence of the rate of shear on the viscosity of the AgI sols, the latter decreasing with increasing shear. Further examination with different sol concentrations and electrolyte concentrations showed the absence of the electroviscous effect, previously known from the theoretical work of Smoluchowski and more recently from that of Booth (63). This is consistent with both theories but because the required correction terms are too small, the effect escapes observation. At higher solconcentrations and with low electrolyte content a new, higher-order electroviscous effect was discovered, caused by the interaction of double layers. A theoretical explanation of the new effect is suggested. At high salt concentrations there remains a hydrodynamic interaction. The concentration by volume being ϕ, for $K = \eta_{rel.}/\phi$ was found a value of 3.55 extrapolating to $\phi = 0$. A discussion of various efforts in testing the theories

of Smoluchowski and of Booth has been given by Dobry (64). She points out that there are no objects which meet all theoretical requirements. Her own measurements on aqueous suspensions of cellulose nitrate (65), carborundum (66), and thorium oxide (67) show mainly the same effects as reported from the work of Harmsen.

Volume effect.—Regarding the viscosity of suspensions containing particles of supposed spherical shape, Olivier (68) pointed out that a plot of $1-1/\eta_{rel.}$ versus ϕ gives a straight line in many cases. This would mean that instead of the formula $\eta_r = 1+K\phi$ (Einstein) an expression $\eta_r = 1+k\phi+k^2\phi^2 +k^3\phi^3+k^4\phi^4+\cdots$ should give a better description.

The flow behavior of glass spheres in water-glycerol mixtures, investigated by Williams (69), was shown by Maron & Fok (70) to obey a relation proposed by Maron, Madow & Krieger (71, 72) and previously applied with success in the case of latex suspensions viz. $\log \eta_{rel.} = b\alpha\phi/(1-\alpha\phi)$, where α and b are constants and ϕ is the volume fraction of the spheres. $1/\alpha$ represents the volume fraction where η reaches infinity. The slope of the η_r versus ϕ plot, as ϕ approaches zero, will be $2.303\alpha b$. Computing this value from Williams' data, one finds 3.15–3.35 instead of 2.5 and this might be the reason why the expressions of Roscoe (73) and of Mooney (74) do not apply to the experimental results. The author suggests that the larger slope indicates an interaction of the glass spheres with these media.

Rheology and stability.—The effect of a magnetic field on the rheological properties has been measured by Harvey (75). Measurements with a rotational viscometer on suspensions of carbonyl iron and magnetic iron oxide in glycerol or linseed oil show that the yield value of the dispersions is enormously increased in a magnetic field. The slope of the shear versus stress plots is only slightly altered. It is clear that the enhanced flocculation is responsible for this effect.

Pryce-Jones (76) has given an exhaustive review of the different rheological states obtained by dispersing fine particles in Newtonian or non-Newtonian liquids, though the phenomenon of thixotrophy is the main subject of this paper. The author describes a great variety of measuring apparatus, illustrating their use by a number of curves. It is shown how the degree of dispersion can be obtained from rheological data after it has been stated that the dispersion increases as we pass along the states: structural viscosity- false body- thioxtropy- dilatancy-Newtonian flow. From this have resulted methods of choosing the composition of a dispersion medium for pigments. Following determination of the point of complete dispersion, a little lower concentration of the solvent with the higher dispersing effect is used to achieve "stability." A general discussion of the flow properties of disperse systems is given in a book edited by Hermans (77). With respect to lyophobic colloids the chapter on "Suspensions" by Roscoe, "Emulsions" by Richardson, and that dealing with "Dilute solutions of impenetrable rigid particles" by Sadron, are interesting.

Other work more or less related to viscosity may be reported here also. In

a series of five papers, Donnet (78) has given, first a general review on the fundamental theories of hydrodynamic methods used in determining the form and the dimensions of rigid particles, followed by a description of the experimental methods themselves. The apparatus for measuring diffusion of translation, birefringence flow of the viscosity, and the sedimentation velocity are discussed together with the electron microscope. Next, the applicability of the hydrodynamic laws is tested on three fully different objects: (*a*) vanadium-pentoxyde, (*b*) tobacco mosaic virus, and (*c*) carbon black.

On the V_2O_5 a rather good agreement is found, the results of the birefringence only giving a value of D (diffusion of rotation), far too low as compared with the expected value. The author looks for an explanation for this discrepancy in the presence of a great number of free vanadic acid ions. The virus particles show a perfect concordance with the theoretically expected behavior; here a verification of the birefringence laws is given for the first time.

The aqueous suspensions of carbon black are well in agreement with theory, as far as diffusion is concerned. The viscosity values are too high, which must be attributed to the electroviscous effect of the charged particles. It is stated that Stokes' law is valid for particles as small as 100 Å. In many respects this work shows a resemblance to that of Scheraga (79) who investigated the double refraction of flow both theoretically and practically.

Optics, X-Ray, Ultra Sound

A contribution to the optics of sols containing small, colorless spheres and having dimensions which differ little from the wavelength of light, was made by Evva (80). A simple method of calculation is given and applied to three separate types of polydispersity. The result is always a lowering of the maximum in the curve of the extinction as plotted against the particle radius. There is a shift to smaller radii too. Typical features of the curves, such as fluctuations or asymmetry effects are smoothed out by the polydispersity.

Later on, Evva (81) investigated the influence of protective colloids on the turbidity of sols, e.g., of AgCl protected by polymethacrylic acid. If the particles are positive because of an excess of $AgNO_3$, the more the polymethacrylic acid is dissociated by increasing pH, the more tightly will it be bound to the silver chloride surface. The turbidity is then slightly decreased.

Scattering of light by much larger particles ($\pi D/\lambda = \alpha$ up to 400) was investigated by Gumprecht & Sliepcevich (82), both theoretically and experimentally. A quantitative relationship between the total scattering coefficient K_t and the apparent or actual scattering coefficient K_a is presented. K_a appears to be a function of K_t and θ, θ being the half-angle of the cone subtended by the light-measuring instrument. The computed K_a values were confirmed experimentally by measurements on prepared disperions of glass beads in water. Further on a method for the measurement of the distribution of particles sizes in polydispersed systems is derived mathematically. According to this method, light transmisssion measurements are combined

with differential settling. The experimental setup is described briefly and an example of an analysis of aerosol, produced by spraying kerosene, is given.

Generally, the interpretation of x-ray diagrams gained by low-angle scattering of diluted colloid systems does not meet with much controversy. A different situation is found regarding the results obtained on close packed systems wherein by most authors, it is believed that the distribution of intensities is altered only slightly compared with the diluted system. Kratky and his co-workers (83a, b) stressed the fact that in a system containing more or less uniform particles imbedded, the "pattern" formed by the particles themselves must be considered. In testing this statement the experimental technique needed many refinements, and now the first results are given by Kahovek, Porod & Ruck (84). The following systems were investigated: xylane from beechwood, soot from naphthalene, nickel, titania, precipitated alumina in different states, and bentonite. The results were checked with electron micrographs and agreed rather well. The diagrams give information, only in a qualitative way about the mean diameter, the inner surface area and the anisotropy of the particles.

To what extent there is any possibility of destroying particle aggregates or even the particles themselves by applying ultrasonic waves was investigated by Gärtner (85). Although these experiments bring no new points of view, it is worth-while to note that cavitation is the main factor causing a dispersing effect. The particles involved were all of an inorganic nature; after each exposure of the suspensions to the ultrasonic field, the particle size distribution was determined by the method proposed by Andreasen. Best results were obtained with a frequency of 500 kc./sec, and with concentrations of about 0.002 gr./cc. It may be noted that well-shaped crystals are destroyed only sporadically; to account for an effect a weak coherence is presupposed.

Surface Area

It has always been an interesting problem to determine the surface area of powders in an absolute manner. During 1953, two methods were proposed, one of which, presented by Karagounis (86), goes back to an old observation made by Ostwald. If a low melting organic compound, e.g., salol, is adsorbed on a powder, there exists a critical surface density beyond which the adsorbed layer can not initiate the formation of crystals in a subcooled mass or in a supersaturated solution of the same substance. It is supposed that this critical occupation of the surface is correlated with the transition of an amorphous film into a more crystalline condensed film of the adsorbed substance on the powder. It is clear that this phenomenon can not be used as a measure in ascertaining the surface area unless the adsorbate is assumed to be spread quite uniformly, and unless an estimation is made of the critical thickness D_{min}. By means of a TiO_2 powder of known surface area (from BET measurements) for *p*-Cl-phenol D_{min} was found to be 13.2 Å. In the case of conducting or semiconducting particles, the method can be extended

by measuring the conductivity of the compressed powder as a function of the adsorbed amount of (nonconducting) substance. A discontinuity in the conductivity was found at the same critical value of the adsorbed quantity as in the nucleation experiments. Payne (87) worked out a method for the determination of surface areas by measuring the relation between the moisture content of the wetted powder and the suction pressure exerted on it. The increase in surface area ΔA of the water can be related to the work performed by the suction pressure, as is expressed by the relation $\Delta A = 1/\gamma \int h dv$ where γ means the surface tension, v the moisture content and h the corresponding suction pressure. If one supposes the contact angle between the solid and the water to be zero and if the suction pressure is not too small then, according to the author, ΔA may be identified with the surface area of the solid. Payne has measured the surface areas of glass spheres by the indicated method. It seems to us that one has to be extremely careful in identifying ΔA with the surface of the solid, especially for substances of complex porosity, as much liquid may be held back in cavities or at points of contact between the particles. With respect to this, mention has to be made of the older experiments of Bartell (88).

From the measurements of the adsorption of gases and vapors on a powder the surface area may be calculated according to different methods. Three of them were indicated by (*a*) Brunauer, Emmett & Teller (BET) (89); (*b*) Hüttig (H) (90); and (*c*) Harkins & Jura (HJ) (91). Schreiner & Kemball (92) applied all three methods to measurements on CuO, ZnO, MgO, and NiO, and found the methods of Brunauer *et al.* and Hüttig to be superior to that of Harkins-Jura; the Hüttig method giving the most reliable results as the equation holds over the greatest range of relative pressures. The adsorption and desorption isotherm were found to be completely coincident, the following vapors being used: CCl_4, n-C_7H_{16}, $C_6H_5CH_3$, n-C_4H_{10}, C_6H_6 and n-C_3H_7Cl. The Brunauer-Emmett-Teller and Hüttig methods show agreement if the Brunauer-Emmett-Teller constant c happens to be high. Again, the computation of pore sizes from physical adsorption data was treated by Pierce (93). For two types of capillaries, one showing hysteresis and the other not, the adsorption mechanism is thought to be different. The method of calculation in using the Kelvin equation is criticized.

An apparatus for sedimentation analysis was designed by Kändler & Miller (94) in which the fractions successively descending are separated by means of movable flat cells attached to the bottom of the vessel. With the aid of a water manometer, leaking of the apparatus when the cells are changed, can be avoided. It is possible to collect the fractions immediately onto glass slides for microscopic examination.

Gels

Earlier in this review, mention was made of silica acid gels in connection with the settling of luminescent screens. Shapiro & Weils (95) introduced a

new technique for the study of the nature and location of the bound water in silicagel. In exposing diborane B_2H_6 to the water-containing gel, measurement was made of the ratio of hydrogen developed to the diborane consumed. For "adsorbed" water this ratio is found to be 6:1, a lower ratio showing the presence of "bound" water. This bound water forms surface hydroxyl groups sufficiently separated from each other that no more than one H atom from each B atom is permitted to react. Although it is indicated that not all OH groups are accessible at low temperatures, a correlation may be expected to exist between the amount of bound water and the specific surface of the gel at higher temperatures. Such a trend has been observed. A method of obtaining dry, undisturbed, clay gel-structures by means of freeze drying [see Hoffman (96)] is described by Call (97). Extreme dehydration results in a distortion of the gel structure, suggesting that hydrogen bonding with water molecules is responsible for the interlinking of the clay crystals.

Tewari, Dey & Ghosh (98) continued studying the nature of hydroxide gels, precipitated under different circumstances from solutions of $AlCl_3$ or $CrCl_3$. The amount of added alkali hydroxide and the temperature were varied. As is usually the case, recrystallization of the precipitates on standing produced a lowered adsorption capacity, but this effect is largely dependent upon the amount of alkali added. After 20 days of aging, a larger absorption of anions was found in gels to which an excess of NaOH had previously been added. The same is true for cations if an insufficient amount of NaOH is introduced. This seems contradictory, as one would expect the gel to be negative in the first case and positive in the second. Tewari (99) also investigated the x-ray diffraction of the gels of $Cr(OH)_3$. The equivalent-precipitate proved to be amorphous but a shift to both sides of the equivalence point caused the gels to be distinctly crystalline. Also differences were found in fluorescence on irradiating with ultraviolet light.

A good deal of experimental evidence on Al-hydroxide gels has been compiled on a paper by Calvet *et al.* (100), where gels generated in an acid medium are compared with those coming from an alkaline solution. Here the former adsorb more anions than do the latter. On the other hand, x-ray analysis reveals the acid gel to be amorphous and the alkali gel to show the structure of pseudo-Boehmite. The authors suppose the anion to stabilize the amorphous state.

Genesis

The formation of colloidal gold, extensively studied already in the early days of colloid chemistry, has recently been investigated by Turkevich, Stevenson & Hillier (101). In gold sols it proved to be possible to separate the stage of nucleation from the following stage of growth. The distribution curve of the particle sizes was studied electron-microscopically and found to be non-Gaussian, which must be due to the kinetics of the nucleation process. The spread in particle size will correspond more or less with the spread in

time of nuclei formation, a nucleus having a transitory existence. As nuclei have diameters of 50 Å or less, nearly one thousand of $AuCl_3$ molecules will be required to build one of them. The authors assume the existence of a sort of precursor of the nucleus, consisting of a macromolecular inorganic-organic polymer which, having once become sufficiently great, might undergo a molecular rearrangement leaving a metallic nucleus apart from the oxidation products of the reduction agent. The particle size distribution would be altered only slightly by the following growth.

Wintgen & Duyster (102) proved that the number of grown particles is strictly proportional to the amount of nuclei added, even when the diameter has been increased to the hundredfold. The paper contains a very elaborate account of all precautions necessary to obtain reliable results. The number of particles was estimated with the classical ultramicroscope; a test using the electronmicroscope would be useful.

The formation and titration of vanadic acid was studied by Hazel, McNabb & Santini (103). In a discussion of the titration curves, the authors conclude a low-molecular weight isopolyacid $H_4V_{10}O_{27}$ to be in equilibrium with the colloid.

The nucleation and growth of silver chloride in its supersaturated solution was studied by Kobayashi (104), who measured the Ag ion concentration electrometrically. Theoretical derviations are given, explaining the observed behavior.

At the symposium "Properties and reactions of carbon" (122nd meeting of the American Chemical Society held at Atlantic City, New Jersey) papers were presented, some of which are of interest for the colloid-chemical behavior of carbon black. Beside the study of pore structure (105) and of graphitization (106) there is much information on the surface area in its dependence on various treatments. On the other hand, Grisdale (107) investigated the formation of black carbon. Electron-microscopic evidence is presented in support of the hypothesis that black carbon, resulting from pyrolysis of gaseous hydrocarbons, is produced through the intermediate formation of droplets of complex hydrocarbons. The droplets consist in part of graphite nuclei. It is suggested that the formation of carbon by the carbonization of solids and by deposition from the gas phase occurs through similar mechanisms.

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CRYOGENICS[1]

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The subject entitled "cryogenics" covers so many fields of investigation of such widely varying interests that a review of this nature cannot adequately treat the whole. Superconductivity and the treatment of magnetic phenomena below 1°K, especially antiferromagnetism, would each require a review of this size. Low temperature physics is not only a field in itself, but is an important tool in the investigation of a multitude of problems in nuclear and solid state physics, few of which can be mentioned here. We, therefore, arbitrarily limit the discussion to certain typical topics, attempting to give the present status, rather than to compile an exhaustive bibliographic treatment.

The third law of thermodynamics, superconductivity, adiabatic demagnetization per se, nuclear alignment, and color centers at low temperatures are not treated; the properties of solutions of He^3 in He^4 and the highly nonideal behavior of mixtures of the two isotopes He^3 and He^4 are discussed in the review of Rice & Morrow and in that of Jones, on isotopes, in this volume.

Fortunately, the editors of *The Philosophical Magazine* have sponsored a series of detailed review articles in 1952 and 1953 on subjects pertaining to low temperature physics; these have appeared in *Advances in Physics*, the quarterly supplement to *The Philosophical Magazine*, and are referred to in the text of this review (1 to 4). They constitute an excellent and timely series.

In general, we are concerned mainly with the properties of liquid and solid helium (He^4 and He^3), the thermal and transport properties of metals and dielectric crystals, and the temperature scale below 4°K.

The Helium Problem

Liquid helium of isotopic mass 4 shows at 2.19°K the peculiar phenomenon of the λ-point, a transition of higher order, involving an over-all entropy change of about $1\frac{1}{2}$ entropy units. Most striking are the abrupt changes in the transport phenomena. He—I, the form of liquid He^4 above the λ-point, shows the small heat conductivity and viscosity of a condensed rare gas, taking into account the marked effect of zero-point energy. However, below the λ-temperature, in the so-called He—II region, the heat conductivity in wide capillaries (larger than ~0.1 mm.) is about 10^8 times greater, exceeding that of copper by orders of magnitude. The heat current is not a linear function of the temperature gradient, but is proportional to its

[1] The survey of the literature pertaining to this review was concluded in December, 1953.

cube root. In very fine slits or capillaries (diameter $<10^{-3}$ cm.), the conductivity is only about 1 per cent of that in the wider capillaries, but again becomes proportional to the temperature gradient. The viscosity (measured at low amplitudes by an oscillating disc method) drops below the λ-point with approximately the seventh power of the temperature.

Three completely new phenomena appear: (*a*) The fountain effect.—If a temperature difference exists between two vessels containing liquid He—II and connected by a narrow opening below the liquid level, a hydrostatic pressure difference arises which exceeds 10 cm. liquid helium per 0.001°K near the λ-point, and decreases with about the seventh power of the temperature. The fountain effect (often called the thermo-mechanical effect) is an analogue to the well-known thermo-molecular effect of Knudsen in gases, and to thermo-electricity. Just as the thermo-electric effect is related to the Peltier heat, an equivalent heat effect occurs when He—II enters or leaves a narrow opening; this is called the thermo-mechanical heat. The relation between the pressure difference ΔP, the temperature difference ΔT, and the thermomechanical heat Q, is the analogue of the Kelvin relation for thermoelectricity: $\Delta P/\Delta T=\rho(Q/T)$ (ρ being the density). With Q assumed to be equal to TS, the relation becomes $\Delta P/\Delta T=\rho S$. This equation was first thermodynamically derived by H. London (5) and was later based on Onsager's reciprocity relation by de Groot (6). (*b*) Film flow.—He—II flows over walls which extend above the liquid surface, equilibrating any level differences. This creep rate (usually called the transfer rate) may be measured by observing the drop of the liquid level in a beaker after the vessel has been lifted out of a surrounding bath. The transfer rate, practically independent of the level difference [Daunt & Mendelssohn (7)] is of the order of 10^{-4} cm.^{3}/cm. circumference/sec. below 1.6°K, and drops to zero at the λ-point. (*c*) Second sound.—Heat pulses are transmitted through He—II in the form of wave propagation and not by means of the diffusion mechanism of heat conduction which occurs in other matter. By sending pulses of heat through a column of liquid He—II it is possible to set up temperature waves, just as pressure waves are propagated in the transmission of ordinary sound (first sound).

The phenomenological theory relating these properties was given by Tisza (8), developing F. London's (9) suggestion that the λ-point might be related to the condensation phenomenon in a Bose-Einstein gas. (He^4, consisting of an even number of nucleons, obeys Bose statistics.) Independently, Landau (10), starting with a different physical picture, arrived at similar conclusions.

Landau and Tisza assume that below the λ-point liquid helium consists of a mixture of two components—interpenetrating fluids—one of which behaves normally, like He—I, called the normal fluid, with a density ρ_n, the other being responsible for the strange transport phenomena, the so-called superfluid component, with density ρ_s. The sum $\rho_n+\rho_s=\rho$, the density of the bulk liquid. At the λ-point, ρ_s becomes zero and $\rho_n=1$. At 0°K, ρ_s is supposed to be 1, and $\rho_n=0$. ρ_n carries the energy, and the entropy of ρ_s is assumed to

be zero at all temperatures. These two "fluids" are assumed to have independent velocity fields, i.e., they move independently, without interfering with each other, at least up to certain limiting relative velocities.

The real nature of these two parts of the fluid is as yet little understood. Near absolute zero, the excitations representing the normal fluid are phonons, the quanta of sound waves (density fluctuations). Around 0.5°K, a new type of excitation contributes to the normal fluid, and therefore to the total specific heat and entropy. This excitation soon becomes the dominant influence at higher temperatures. Landau describes the excitation as being due to rotons; they may be described vaguely as vortices comprising a few atoms only.

The appearance of the superfluid component is responsible for the tremendous change in transport phenomena below the λ-point. For example, since the transfer of momentum involved in viscosity measurements can take place only to the normal fluid, and not to the superfluid, the viscosity determined in the classical manner from the momentum transfer and the density of the bulk liquid has to drop proportional to the rate with which ρ_n decreases with temperature (approximately as T^4). Also, the high heat conductivity occurs in a manner similar to that of the high heat conduction of dissociating gases. The atoms carry from hot to cold regions not only the small amount of kinetic energy intrinsic to each atom, but also a considerable excitation energy. Due to superfluidity, the mean free path for the process is extremely long, producing a tremendous heat transport.

In this picture the fountain effect corresponds to an osmotic pressure. The normal part of the liquid ρ_n constitutes the solute, ρ_s the solvent, and the narrow opening is the semipermeable wall which allows the superfluid to pass but retains the normal fluid. Since ρ_n and ρ_s are functions of the temperature, a difference in temperature between the two vessels means a difference in concentration, and hence a difference in osmotic pressure.

Since the action of the van der Waals forces of any solid wall on helium atoms is much stronger than the He—He interaction, liquid helium wets all surfaces of contact. As soon as superfluidity appears below the λ-point, the superfluid can move without friction in the film and thus produce the unusually fast creep.

As the superfluid part ρ_s and the normal part ρ_n can move independently, ρ_s and ρ_n can move not only in phase with each other, producing changes in material density, i.e., ordinary sound waves, but also in opposite phase, producing second sound. The total density $\rho_s+\rho_n=\rho$ remains constant, but the ratio ρ_n/ρ_s varies. Since this ratio determines the energy content, the waves consist of changes of energy density. The physical reality of this picture has been demonstrated by Pellam and co-workers (11) by putting a Rayleigh disc in the node of a second sound wave and showing that the torque exerted on the disc is due to the motion of ρ_n and ρ_s in opposite directions. The important ratios ρ_s/ρ and ρ_n/ρ can be derived from the velocity of second sound.

The status of the liquid helium problem has been treated recently in a

series of detailed review articles by Dingle (1), Atkins (2), Pellam (12), and Long & Meyer (4).

The main contribution in 1953 to the theoretical understanding of liquid He^4 is due to Feynman (13). Previous to this work, a condensation phenomenon had been rigorously derived only for an ideal Bose-Einstein gas. No theory of liquids exists which could be considered as even approximately rigorous. It has been seriously doubted that the condensation effect could occur in the liquid state, for which the particle interactions are so strong. (In a solid, the particles lose identity due to the strong forces of interaction, and the statistics of free particles become unimportant.)

Thus, the calculation of equations of state, boiling points, and the virial coefficients by de Boer and co-workers (14) using his generalized theorem of corresponding states, arrived at good agreement for He^4 and excellent predictions for He^3 (Fermi-Dirac statistics) without consideration of the statistics.

Feynman studied the quantum-mechanical behavior of strongly interacting atoms of He^4, and derived from first principles that, in spite of the great interatomic forces, liquid He^4 should exhibit a transition analogous to the transition in an ideal Bose-Einstein gas, thus supporting the original suggestion of F. London (9). He argued that, in a liquid-like quantum system, the strong particle interactions do not prevent the particles from moving freely among each other. The effect of the other atoms is not to offer a potential barrier, as in the case of a solid, but a kind of kinetic barrier, essentially changing only the effective mass of the moving atoms, because the other atoms can move out of the way. The particles retain sufficient independence so that the statistics are important.

Feynman's partition function showed that a transition was to be expected (although of the third order) and that the symmetrical statistics of the particles were involved in a very essential way. Thus the Feynman theory, though as yet qualitative only, provides strong fundamental theoretical support for the physical picture involved in the detailed phenomenological theories which preceded it.

In a second paper (13), Feynman treated qualitatively the behavior of liquid He^4 below 0.5°K from an atomic point of view, and showed that the lowest states are phonons (compressional waves). In his view, the specific heat should vary as T^3 in this region (as indeed is found experimentally), and long-range motions which leave density unaltered are impossible for particles of Bose statistics, since they simply permute the atoms. The reader is referred to the original papers for details.

The nature of the excitations in liquid He—II has been discussed by H. A. Kramers (15), Dingle (16), Ward & Wilks (17), Temperley (18), and Kronig (19). Kronig & Thellung (20) attempted to write the hydrodynamic equations for He—II as those of a nonviscous fluid in terms of field theory.

Among the experimental contributions to the helium problem, we mention the following.

Guttman & Arnold (21) found that the radioactive isotope He^6 does not participate in the superflow of He^4 through narrow slits. This result is consistent with the idea that superfluidity is a consequence of the Bose-Einstein statistics. He^6 itself obeys Bose-Einstein statistics; in a dilute mixture in He^4, however it is a strange atom, statistically distinguishable, and therefore cannot participate in the statistical degeneration of He^4.

The specific heat of liquid He^4 has been redetermined by H. C. Kramers, Wasscher & Gorter (22) and by Hull, Wilkinson & Wilks (23). Below 0.6°K the specific heat varies as T^3, fitting therefore a Debye law, and confirming the assumption that near 0°K phonons are the dominant excitations. At higher temperatures, the specific heat rises much more rapidly (approximately as T^6), indicating the appearance of a new form of excitation. The new specific heat data yield entropy values which remove the previous discrepancy between the thermal measurements and fountain effect data (24).

Confirmation of this may be found in the values of ρ_n/ρ as a function of T, as derived from second sound velocities by de Klerk, Hudson & Pellam (25). At temperatures up to 0.55°K, ρ_n/ρ increases proportional to T^4; at higher temperatures the dependence becomes as T^6; a double logarithmic plot of ρ_n/ρ versus T shows two distinct branches, denoting the predominance of phonons and rotons, respectively.

Special efforts were devoted to the measurement of the velocity of second sound below 1°K. Landau (10) had predicted that, since phonons were the main excitations at very low temperatures, at 0°K the second sound velocity C_{II} should be $2/3\ C_I$, the first sound velocity. Since $C_I = 360$ m./sec. at 0°K [Atkins & Chase (26)], in the limit C_{II} should then not exceed 240 m./sec. However, most experiments in this region—de Klerk, Hudson & Pellam (27), Mayper & Herlin (28) and H. C. Kramers *et al.* (29)—have yielded higher values. It is true that the energy imput to produce measureable second sound signals at these low temperatures is high compared with the vanishing heat capacity; therefore, the production of shock waves cannot be excluded. However, even the second sound velocity extrapolated to zero amplitude (minimum energy imput) is still too high. The most plausible explanation seems to be that the mean free path of the phonons becomes greater than the dimensions of the vessel. In this case, phonon density variations would traverse the vessel, not with phase velocity, but with their own much higher actual velocity—C_I—the velocity of ordinary sound.

The attenuation of second sound has been measured by Pellam & Hanson (30) and by Atkins, Edwards & Hart (31); it seems to be consistent with Khalatnikov's (32) view that the dissipation of energy is caused by the "normal" thermal conductivity of the liquid, namely by the inelastic collisions of phonons.

Hollis-Hallett (33) carried out a very careful investigation of the viscosity of liquid He—II, using a rotating cylinder viscosimeter. At low velocities, the results agree with the simple picture of the two-fluid model; however, the deviations observed at higher speeds do not agree with the attempted exten-

sions of the two-fluid hydrodynamics by the introduction of nonlinear mutual friction terms, as proposed by Gorter & Mellink (34).

Further attempts to gain insight into the λ-phenomenon were made by measuring the scattering of x-rays, of ultraviolet light, and of slow neutrons by liquid helium. (The condensation phenomenon of an ideal Bose-Einstein gas would produce differences in scattering above and below the condensation temperature for light and for neutrons, and critical opalescence at the transition temperature.) Lawson & Meyer (35) measured the scattering of light by liquid helium, using a high pressure Hg arc lamp. Within the accuracy of about 20 per cent, no increase in scattering could be found at the λ-point. Although extremely small, the light scattered at an angle of 90° by the liquid, between 4.2° and 1.5°K, could be accounted for "classically" by using the experimental compressibilities in the equations for Rayleigh scattering. Reekie & Hutchison (36) confirmed Reekie's former result, and that of Keesom & Taconis (37), that there is no difference in the x-ray scattering between He—I and He—II. They obtained a typical liquid pattern, from which they derived that 4 atoms are at an average distance of 3.3 Å, 6 more at 4.4 Å, and possibly 8 at 5.4 Å. A crystal structure having a similar distribution can be derived from a fcc crystal by removing eight of the twelve nearest neighbors.

Neutron scattering has been measured by London & Egelstaff in Harwell, England (38), by Henshaw & Hurst at Chalk River, Canada (39), and by Dash, Sommers & Goldstein at Los Alamos (40). No effect of the large inelastic scattering expected for an ideal Bose-Einstein gas [Goldstein, Sweeney & Goldstein (41)] has been observed. Further experiments are planned, using neutrons of longer wavelength than those of the present work (3 to 16 Å); these should give more detailed information on the momentum distribution in the liquid.

The helium film.—Considerable attention has been paid to the helium film, its thickness, and its mobility as shown by the transfer rate. Boorse and co-workers (42) developed a dielectric capacity gauge for measurement of the liquid level, in order to determine the transfer rate in and out of beakers which were not transparent, so that the usual direct visual observation could not be used. The result of these investigations is that the transfer rate is independent of the material of the beaker, i.e., of the substrate over which the film flows; the flow is also very little influenced by the surface finish. There is a scatter of about 10 per cent in the data, which, however, appears to be rather accidental.

Picus (43) measured the transfer rate at very small level differences (0.01 to 1 mm.) by displacing the liquid inside a beaker with a plunger in a controlled manner. He found that the flow can be described by equations of the same type as those used by Atkins (2) to describe the oscillations of the liquid level in a beaker at the end of a transfer experiment, when, due to its kinetic energy, the film overshoots the equilibrium level and begins to oscillate about it. However, the constants Picus needs to fit these equations numerically to his data are distinctly different at the beginning of the flow as compared to

a later stage, such as the steady-state reached after some minutes. He concludes that the film thickness and its dependence on height are different for the static film (at rest), and for the moving film.

The thickness of the film has been measured by two methods. Jackson and co-workers (44) have refined their optical interferometric method. Bowers (45) used a sensitive quartz microbalance [developed by Bowers & Long (46)] for an intensive study of the film thickness, by weighing the amount of helium on the surface of an aluminum foil hanging above the liquid. In his first paper he confirmed that at pressures P greater than about 70 per cent of the saturation pressure P_0, the number (n) of layers adsorbed follows the relation derived by Frenkel (47), Halsey (48), Hill (49), and McMillan & Teller (50): $-\log P/P_0 = K/n^3$, which is a consequence of the fact that the van der Waals forces between the wall and the adsorbed atoms decrease with the third power of the distance. The constant K should vary approximately as $1/T$ [McMillan & Teller (50)]. It seems to increase more rapidly below the λ-point, but no break or discontinuity occurs at the λ-point, within the accuracy of the data. K varies from $\sim$8 at the boiling point to $\sim$60 at 1.6°K.

The film in contact with saturated vapor (at P_0), but not in contact with the liquid surface, is about 55 layers thick. Then, as soon as the specimen has contact with the liquid surface below it by means of a wire of 0.005 cm. diameter, the film thickness increases to $\sim$150 layers below the λ-point, independent of temperature, whereas only 15 layers were found above T_λ under similar conditions. This great difference in film thickness on a specimen with and without contact with the liquid surface is probably due to minute temperature gradients, so that the specimen is at a slightly higher temperature when it is not physically in contact with the liquid; this would cause the film thickness to decrease. Bowers found that the film thickness was extremely sensitive to thermal radiation.

In Bowers' work, the thickness was proportional to $1/h^{1/2}$, where h is the average height above the liquid. By combining the van der Waals third power relation with the gravitational potential, Schiff (51) and Frenkel (52) predicted that the thickness should vary as $1/h^{1/3}$. Bijl, de Boer & Michels (53) had suggested that, quantum-mechanically, the energy of the helium film should depend strongly on the thickness, and a formulation of this led to a height variation of $1/h^{1/2}$. The situation is still unresolved.

The behavior of the unsaturated helium film, i.e., the film in equilibrium with the gas phase at a pressure P which is less than the saturated vapor pressure P_0 at any given temperature, has been reviewed by Long & Meyer (4). There are strong deviations from the usual adsorption isotherm, due to the high zero-point energy, the typical He—II phenomena appear (including superfluidity and high heat transport, even in films of very few statistical layers) and the thermal properties of the films, particularly the entropy and specific heat, are markedly different in the He—II region from those of ordinary adsorbed films.

Brewer & Mendelssohn (54) have measured the adsorption of helium on

glass at temperatures in the He—II and He—I regions, obtaining results which disagree with those of other investigators [compare also Tjerkstra *et al.* (55)]. Their data have been criticized by Long & Meyer (56) who found that they could not satisfy the criteria of thermodynamics with the data. Brewer and Mendelssohn have discussed their results in terms of a special "cluster" theory, which however, seems difficult to reconcile with thermodynamics and with the superfluid behavior of the adsorbed films.

Simon and co-workers (57) have made an elegant and extensive study of the melting curve and other properties of solid helium. Helium is the best substance available for a study of the melting curve, since the melting process can be followed to extremely high relative temperatures. It has been measured up to 26°K (five times the critical temperature) and it is intended that the investigations be carried up to liquid nitrogen temperatures (78°K). Up to 26°K and 3000 atm., there is no indication of a critical point in the melting process. ΔV remains practically constant, whereas ΔS increases with P and T. The tentative conclusion of Simon (58) has been confirmed, namely that it is impossible to melt a substance by adiabatic reversible compression, since such a process only leads further into the stability range of the solid. A first-order transition, with a transition heat of 0.08 cal./mole, was discovered, the transition curve intersecting the melting curve at 14.9°K.

The helium isotope of mass 3.—The helium isotope 3 consists of an uneven number of nucleons and therefore obeys Fermi-Dirac statistics. As the λ-point phenomena in liquid He^4 are a consequence of the Bose-Einstein statistics, no such phenomena should be expected in He^3, and none have been observed in the liquid down to 0.1°K. However, the influence of the zero point energy is still greater than in liquid He^4. The smaller the mass, the greater is the energy of a particle according to the uncertainty principle, if it is confined within a given space. Thus, the density of liquid He^3 is only 0.06 gm./cc. at its boiling point, 3.2°K (59), and its heat of vaporization is only 5.3 cal./mol. at the boiling point (60), whereas the mutual attraction due to the van der Waals forces should be about the same as in He^4, which Simon (61) estimated to be about 70 cal./mol. The zero-point energy therefore almost completely compensates the van der Waals attraction of the atoms. Just as He^4, He^3 has no triple point: it does not solidify under its own vapor pressure. The lowest observed pressure necessary to solidify the liquid is about 30 at 1°K (62).

In spite of the absence of λ-point phenomena, the influence of statistics on He^3 is of great interest. It was already mentioned that de Boer and coworkers (14) were able to predict the boiling point and the critical temperature of He^3 with great accuracy, without taking statistics into account. An ideal Fermi-Dirac gas of the density of liquid He^3 should show a degeneracy temperature around 4.5°K. Below this temperature, the statistics, i.e., the Pauli exclusion principle, should enforce alignment of the nuclear spins. For solid He^3, one would expect that the particles lose their identity, and the statistics their influence, so that nuclear alignment can only be achieved by

the interaction of the nuclear moments themselves, which is exceedingly weak and should not be effective above $\sim 10^{-4}$°K. A lack of nuclear alignment creates a contribution of $R \ln 2$ to the entropy. Pomeranchuk (63) pointed out that if the liquid shows degeneracy, whereas the solid does not, the entropy of the solid would become greater than that of the liquid, and this change of sign in ΔS must produce a change of sign of the slope of the melting curve as required by the Clapeyron equation. This means that the melting pressure curve would have a minimum, and should increase with decreasing temperature below a certain temperature. Experiments show that at least down to 0.42°K the entropy of the liquid still exceeds $R \ln 2$ (64), suggesting that the degeneracy of the Fermi-Dirac statistics has not yet set in. Fairbank *et al.* (65) confirmed this thermodynamic result by measuring the nuclear magnetic susceptibility. Down to 1.2°K the susceptibility follows a Langevin-Curie $1/T$ law for independent non-degenerate moments. The direct determinations of the melting curve by Weinstock, Abraham & Osborne (62) are inconclusive about an eventual change of sign in the slope of the melting curve. They used the blocked capillary method, which will always produce a block at the minimum melting pressure—if it exists, as the inevitable temperature gradients would allow the temperature corresponding to the minimum melting pressure to be present.

The amazing fact that the two isotopes He^3 and He^4 form highly non-ideal solutions with a considerable heat of mixing, due to their great difference in density as a consequence of the different influence of the zero-point energy, is discussed in the article by Rice & Morrow in this volume.

The properties of He^3 were reviewed in detail by Daunt (3).

The temperature scale below 4°K.—The practical temperature scale in the range from 1° to 4°K is coupled to the vapor pressure of liquid helium, which is about 0.01 mm. Hg at 1° and reaches 760 mm. at 4.2°K. Until sufficient pure He^3 is available to all experimentalists, the role of He^4 as a thermometric substance is unchallenged. The much higher vapor pressure of He^3 would allow its use as a thermometric substance down to almost one-half degree lower in temperature than is the case for He^4.

The temperature scale has been established down to 1.2°K by measuring the second and third virial coefficients of helium gas and extrapolating to zero density, using a gas thermometer. This work was started by Keesom and co-workers (66). Bleaney & Simon (67) derived the vapor pressure curve of He^4 below 1.6°K by combining all known thermodynamic data and evaluating the Sackur-Tetrode equation. Kistemaker (68), who had extended the vapor density measurements down to 1.2°, used a similar method and came to the conclusion that the so-called 1939 temperature scale (which was based on a combination of the Bleaney and Simon values up to 1.6°K and Keesom & Walstra's (66) gas density measurements at higher temperatures) was probably uncertain up to 14 milli-degrees, especially in the neighborhood of the λ-point. However, the "conventional" temperature scale, compiled by Shoenberg & van Dijk (69) in the form of vapor pressure tables for liquid He^4,

did not take Kistemaker's result into account and even smeared out the small dent in the vapor pressure curve produced by the λ-point. Roberts & Erikson (70) have remeasured the temperature scale magnetically in this region, confirming Kistemaker's finding. In spite of the fact that these corrections are not yet officially accepted, they are widely used in more detailed investigations of temperature-dependent properties, especially in establishing the vapor pressure curve and the entropy of He^3, e.g., by Osborne *et al.* (60, 62, 64).

Below 1°K, the situation is worse. No substance exists which can even unofficially be considered as a thermometric standard. So long as a paramagnetic substance obeys the Curie law, i.e., its susceptibility varies as $1/T$, and this range extends into the region above 1°K, the usual procedure consists in calibrating the susceptibility above 1° against the helium vapor pressure curve and then using the constants to evaluate temperatures below 1°K. In this way, temperatures down to 0.1°K can be established with reasonable accuracy and certainty. Two substances are very useful in this region: potassium chrome alum and copper potassium sulphate. Detailed data are given for both by Garrett (71).

However, the Curie law is only valid so long as kT is substantially greater than the energy difference between the levels of the electron spins (level splitting). At lower temperatures, the susceptibility reaches a maximum and starts to decrease again, and becomes also a function of the measuring field, so that no unique relationship exists between susceptibility and temperature, and the susceptibility itself loses its value as a thermometric parameter.

The temperature is usually rigorously determined from $\Delta Q/\Delta S = T$, by a magnetic Carnot cycle. The lowest temperature established in this way is 0.0014°K, measured by de Klerk, Steenland & Gorter (72). The Dutch thesis of M. J. Steenland (Leiden, 1952) is an excellent survey of the field [compare also de Klerk (73)]. Giauque (74) has critically reviewed the different methods used to supply an exactly known amount of heat ΔQ uniformly to the paramagnetic salt [discussed also by Kurti & Simon (75) and by Platzman (76)] and emphasized that this source of uncertainty can be avoided altogether. The temperature is determined by $T = (\delta H/\delta S)_{H_m}$; from $TdS = dH + IdH_m$ (I being magnetization and H_m the magnetic field) it follows for isentropic demagnetization that $\Delta H = -IdH_m$. If, therefore, the relative heat content H can be measured at temperatures above 1°K, it can be determined at any point below 1° which is reversibly accessible by adiabatic demagnetization without introducing heat, since the paths are isentropic, starting from known entropies determined above 1°K.

The great problems at these low temperatures are heat contact and thermal equilibrium even within the specimen. Exact measurements which can be interpreted from an atomistic point of view require single crystals in the form of spheres or ellipsoids. Even single crystals yield slightly different values for the complex susceptibilities after having been warmed up to room temperature, and require essentially a redetermination of the temperature

scale every time they are used. Also, nonuniform heat leaks can produce serious temperature gradients in single crystals during the experiments. However, the use of single crystals is extremely limited, and its main value lies in determining the magnetic properties of the crystals themselves.

A substance is needed which allows not only the cooling of any matter we want to investigate to very low temperatures, but also the determination of the temperature of the system. The problems of heat contact and thermal equilibrium seem at the moment to rule out the use of single crystals for this purpose. A feasible technique used to cool specimens down to low temperatures by adiabatic demagnetization consists in imbedding the specimen, or copper vanes leading to the specimen, in a powdered paramagnetic salt and pressing the assembly in a die. In this way satisfactory heat contact can be achieved to temperatures as low as $\sim$0.1°K; however, the strained polycrystalline paramagnetic salt is far from suitable as a thermometric standard. No real solution of the problem seems in sight, and there is not even an attempt made to establish a temperature scale below 1° based on established properties of a standard thermometric substance. The accuracy to which the lowest temperatures reached with single crystals are known is only about 25 per cent.

Heat Capacities of Metals, Dielectric Crystals, and Semiconductors

This work is of interest because of its relationship to theories of lattice vibrations, the band theory of metals, and the behavior of semiconductors at low temperatures. From heat capacity data at sufficiently low temperatures (usually in the liquid helium region) experimental tests of the detailed calculations on lattice vibrations may be made. For metals, the electronic and lattice contributions to the heat capacity can be separated and, from the values of the electronic heat capacity term γ thus obtained, conclusions can be derived regarding the density of states, $N(E)$, at the Fermi surface. From the simple band theory of metals, the electronic specific heat is given as

$$C = \gamma T = \frac{2}{3}\pi^2 k^2 N(E) T$$

in cal./deg./cm.^{3}, where $N(E)$ is the number of electronic energy states per unit energy range per unit volume at the Fermi level.

However, it is often difficult to separate the lattice and electronic heat capacities, because frequently the Debye characteristic temperature θ_D is not constant at the lowest temperatures of measurement, and, further, the density of states $N(E)$ is sensitive to impurities and to strains in the specimen, thus affecting the apparent value of γ. Nevertheless, the γ values so determined provide valuable data for the admittedly inadequate theoretical treatments.

Determinations of the electronic heat capacity for metals at temperatures below 1°K would be quite useful, because at these temperatures the lattice

heat capacity is usually so small that it can be ignored, thus removing one source of uncertainty which exists in the measurements at higher temperatures. To date, few such measurements have been reported.

In addition, there is great interest in the thermal properties of magnetic substances, such as a large variety of paramagnetic salts which show anomalies in the heat capacity due to splitting of the energy levels of the magnetic ions by dipole-dipole interactions, by Stark splitting from the crystalline fields of the surrounding ions of the lattice, or which, due to cooperative phenomena, develop antiferromagnetism. Since these are primarily of interest in the study of the magnetic behavior, and need other data, such as susceptibilities and microwave absorption for detailed analysis, the heat capacity work on such salts will not be reviewed here.

Keesom & Pearlman (77) have measured the heat capacity of a single crystal of KCl below 4°K, and find a T^3 dependence (Debye law) with $\theta_D = 233°$, in agreement with elastic constant and vibrational spectrum data. They also report measurements on Ge below 4°K (78). Keesom, Lark-Horowitz & Pearlman (79) have investigated the effects of neutron bombardment on the low temperature atomic heat of Si. The lattice defects created by neutron bombardment markedly decreased the already small contribution of the degenerate electron carrier gas, due to carrier trapping by the lattice defects; the effect could be destroyed by thermal annealing.

The heat capacity of diamond has been remeasured by De Sorbo (80), with results considerably different from the older data of Pitzer (81); there seems to be some evidence that different samples of diamond, of varying purity and crystalline perfection, give rather widely varying values of θ_D. de Sorbo reports data on Se down to 15°K and also finds that the low temperature heat capacity of graphite obeys a T^2 law (82).

Busey & Giauque (83) report data on Hg from 15° to 300°K. Hill & Smith (84) measured the heat capacity of Be from 4° to 300°K; the old anomaly at 11°K is apparently nonexistent. Dworkin, Sasmor & Van Artsdalen (85) determined the heat capacity of boron nitride up to 80°K, and find that C_v is proportional to T^2 up to $\sim$60°K, in agreement with a Debye function ($\theta_D = 348$°K) for a layered (two-dimensional) structure.

Clement & Quinnell (86) have carried out a very careful investigation of the atomic heat of In below 20°K, from which they derived the electronic and lattice contributions.

Horowitz & Daunt (87) measured the heat capacities of W and Mo from 1° to 77°K, deriving values of θ_D and the electronic term from their data. In particular, the γ value for W is radically lower than that obtained from the previous work of Silvidi & Daunt (88). The authors apply their data and those of previous workers to a discussion of the density of states in the transition elements.

Hoare, Matthews & Walling (89) have carried out interesting investigations on a series of Pd-Ag alloys ranging from pure Pd to $\sim$50 per cent Ag. Magnetic susceptibilities were measured in the range 20° to 290°K, and heat

capacities were determined from 11° to 20°K. The results were used to deduce γ, and though the data were not considered to be of high precision for alloys above 15 per cent Ag, the authors were able to deduce the band form for Pd. Experiments on such alloy systems at much lower temperatures would be very desirable.

Mendoza (90) has proposed a method of determining heat capacities of metals at very low temperatures by measuring the velocity of propagation of temperature oscillations along a rod, thus obtaining the thermal diffusivity (ratio of thermal conductivity to heat capacity). Waldron & Herlin (91) have independently applied a similar method to a study of the thermal conductivity of Mg, for which the heat capacity is known.

Transport Phenomena at Low Temperatures

Heat conductivity of dielectric solids.—The heat conductivity of dielectric solids has been intensively studied in the past few years, especially by a group at the Clarendon Laboratory in Oxford. The experimental results and the status of the problem are presented in an excellent review by Berman (92). In dielectrics, heat is carried by elastic (sound) waves (phonons). The theory of thermal resistance due to the inelastic scattering of the phonons (Umklapp processes) was developed by Peierls (93). At low temperatures the theory predicted the thermal resistance to decrease exponentially with T. According to the well-known kinetic theory equation, the conductivity is given by the relation $k = 1/3cvl$, where c is the specific heat, v the velocity, and l the mean free path. At low temperatures, the dominant term representing l is $Te^{-\theta/2T}$, where θ is the Debye temperature [compare Klemens (94)]. However, this exponential increase in conductivity (due to the increase in mean free path) is limited by size effects, because the mean free path of the phonons obviously cannot exceed the dimensions of the specimen. At still lower temperatures, therefore, l becomes constant, and the conductivity becomes proportional to the specific heat, which varies as T^3 for a Debye solid. In this region the motion of the phonons becomes an analogue to the flow of a Knudsen gas, scattering occurring only at the walls, in the ideal case. The theory for this limiting case was first given by Casimir (95) for the simple case of an infinitely long cylinder; the treatment was later refined by Berman, Simon & Ziman (96), who took into account the finite length of the specimen and the possibility of specular reflection of the phonons at the wall. Despite the fact that there remain some discrepancies between experiment and theory, especially the height of the maximum in the conductivity-temperature curve, the theoretical predictions are quite well confirmed. Figure 1, taken from Webb & Wilks (97) shows strikingly how the predictions of theory are confirmed for extremly different substances, ranging from sapphire to solid helium. These considerations were made for ideal crystals, and the experimental verification has been achieved with the best single crystals available in each case. The observed discrepancies are probably due to lattice defects and impurities which contribute to phonon scattering; however,

their influence on the thermal resistance has not yet been formulated in a satisfactory quantitative manner.

Heat conductivity of metals.—The heat conductivity of metals presents a still more complex problem. Besides the heat carried by phonons (as in dielectric crystals), the conduction electrons contribute to the heat transport,

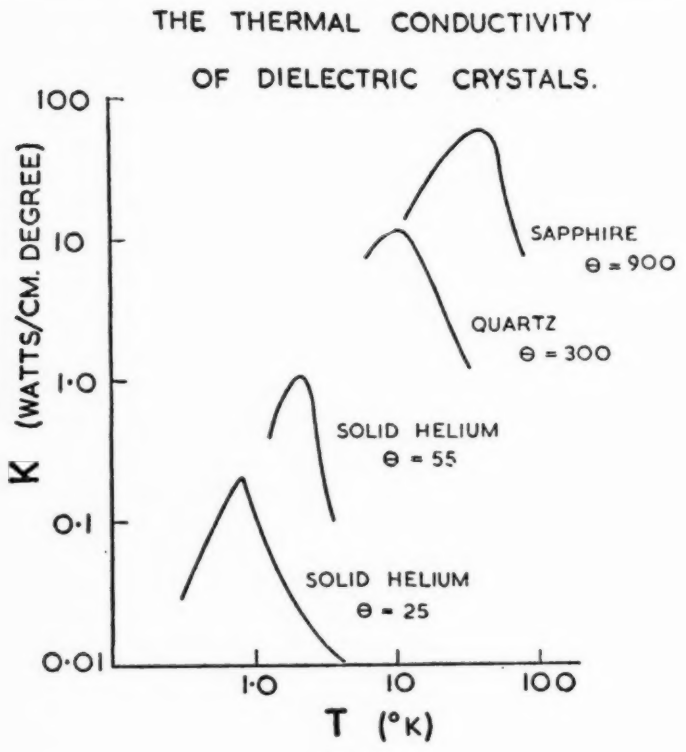

FIG. 1

often in a dominant manner. However, the presence of free electrons in a metallic lattice may change considerably the heat conduction of the lattice itself (phonons), because phonons may be scattered by the free electrons, often even much more than by phonon-phonon processes; thus, the mean free path of the phonons in a metal is quite different from that in a dielectric solid.

The theory of heat conduction in metals has been developed by Wilson (98), Makinson (99), and Sondheimer (100). In spite of the strong mutual

scattering of phonons and electrons, the heat conductivity k of a metal can be written arbitrarily as the sum of the conduction due to the electrons, k_e, and that of the lattice k_l. At sufficiently low temperatures (below $\theta/10$), as Hulm (101) has shown, the lattice resistance ($1/k_l$) in Makinson's theory may be written as a sum of terms:

$$1/k_l = A/T^2 + B/T^3 + CT$$

where A, B, and C are constants. The first term on the right-hand side arises from the scattering of phonons by electrons, the second from the scattering by crystalline boundaries, and the third from that by lattice defects and impurity atoms. For good single crystals, the first term is dominant at low temperatures.

At temperatures lower than $\theta/20$, the resistance to the heat transport by electrons, $1/k_e$, reduces to $1/k_e = \alpha/T + \beta T^2$, where the first term on the right represents scattering of electrons by impurities and the second the scattering by phonons. In the low temperature region for which the electrical resistance of the metal reaches its residual value (i.e., the electrical resistance is determined by impurities—lattice defects and/or impurity atoms), the first term is dominant.

The theory and the experimental results are discussed in the review of Olsen & Rosenberg (102). The experiments show pretty well the temperature dependency expected by theory; however, serious discrepancies exist with respect to the absolute values. The number of free electrons in the metal, derived from the heat conductivity data, is sometimes an order of magnitude smaller than that expected from the valency of the metal. White and coworkers (103) made a careful study of the thermal conductivity of Au, Ag, and Mg at low temperatures.

For metals in the superconducting state, the situation becomes still more complicated. The superconducting electrons now make no contribution to the heat transport, so that k_e is reduced by the ratio of electron population in the superconducting state, at a given temperature. However, k_l increases in the superconducting state, since also the superconducting electrons are not available for phonon scattering; thus the phonon mean free path is increased. The occurrence of superconductivity can therefore decrease or increase the heat transport, depending on the relative importance of electronic or lattice conduction. If electronic conduction is dominant, the heat transport in the superconducting state can become much smaller than that in the normal state of the metal at the same temperature. This fact has been used in the development of a "heat switch" which uses a superconductor as the thermal link; by destroying superconductivity by an applied magnetic field (a few hundred oersteds are often sufficient), the conductance of the link is increased by orders of magnitude (104, 105, 106).

Electrical conductivity at low temperatures.—We treat here only the case of nonsuperconducting metals.

The electrical resistance of an ideal, infinite metallic single crystal should

approach zero at the lowest temperatures, since the main reason for the resistance, the scattering of electrons by phonons, vanishes at T approaches zero, since the irregularities of the lattice due to thermal vibrations also vanish. Actually, the resistance remains finite, with a residual value essentially independent of the temperature. This residual resistance is due to the scattering of electrons by impurities and lattice defects. Therefore, the absolute value of the residual resistance depends on the quality of the crystal; it is lowest for the purest crystals with the smallest number of lattice defects.

One problem besides the phenomenon of superconductivity still remains more or less unsolved, namely the minimum in the electrical resistance at low temperatures, originally observed for gold by de Haas, Casimir & van den Berg (107). Below a certain temperature (around 2°K), the resistance did not remain constant, but actually rose with falling temperatures. Slater (108) has suggested that such behavior might be due to a rearrangement of the gold lattice, such that an energy gap occurs in the occupied Brillouin zone just at the top of the electron distribution (Fermi level), thus making gold essentially an intrinsic semiconductor. Croft *et al.* (109) have measured the resistance of gold wires down to 0.006°K. The total observed increase in resistance above the minimum value was only 3 per cent, whereas the quasi-semiconductor picture would lead to an exponential increase.

From the work of MacDonald *et al.* (110), Mendoza & Thomas (111), and Herlin and co-workers (112), it seems fairly certain that the resistance minimum at very low temperatures is due to impurities, at least for certain metals. Herlin (113) was able to demonstrate that the minimum in magnesium is due specifically to contamination by manganin. MacDonald and coworkers (110) showed that the resistance minimum in gold is produced by Sn, C, or Bi, but not by Ni or Ag. The mechanism by which these small amounts of impurities produce the resistance minimum is not yet fully understood. Gerritsen (114) and Korringa & Gerritsen (115) studied the electric resistance and its dependence on magnetic fields of dilute alloys of the transition metals. They attempt to explain their results in terms of extra states near the Fermi level produced by the impurities.

Magnetic "Refrigerators"

A constant-temperature experimental chamber for the temperature region below 1°K would be quite useful for many purposes. At present, all the experimenter can do is to cool his apparatus to some low temperature by adiabatic demagnetization techniques, and then make measurements while the system is warming at a given rate, which may be small or large, as determined by the limitations of the system.

In principle, a refrigerator can be devised from the use of a paramagnetic salt as the working substance, connected by appropriate thermal "switches" either to a high-temperature reservoir (presumably a bath of liquid helium at $\sim$1°K) or to an experimental chamber which is periodically cooled by the salt, through cyclic magnetization and demagnetization of the salt.

Preliminary designs for such refrigerators have been reported by two groups of workers. Collins & Zimmerman (116) have devised a cyclic demagnetization apparatus which maintains the temperature of a sample at 0.73°K, with the heat sink at 1.13°K; the thermal switching was attained mechanically. Heer, Barnes & Daunt (117) describe progress on a heat engine in which the working substance is a paramagnetic salt, with the thermal "valves" consisting of superconducting metallic links. With this device, temperatures down to 0.3°K were maintained.

While the performance of these systems is not yet capable of providing a very constant temperature environment, it should be possible in the near future to utilize such techniques to provide a good isothermal system for experimental investigations; this, however, will be useful down to ~0.1°K only, since the thermal conductivity of the lattice below 0.1° is such that thermal equilibrium will be extremely difficult to attain.

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NUCLEAR MAGNETIC RESONANCE[1]

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Spectroscopy has long been an effective way to study the structure of matter. And the development of radiofrequency spectroscopy is rapidly filling gaps in the electromagnetic spectrum previously unused for structural investigations. During the past few years spectral phenomena have been observed from audiofrequencies to where microwaves join the far infrared. These discoveries extend in a wide variety of interesting directions, some as yet ill-defined. But several main branches are distinguishable: electronic paramagnetic resonance, nuclear magnetic resonance, pure quadrupole spectroscopy, and ferro- and antiferro-magnetic resonance. The most fully developed branch is the microwave spectroscopy of gases which is reviewed in another section as well as in preceding volumes.

Last year's review by Dailey (1) included pure quadrupole spectroscopy and touched very briefly upon nuclear magnetic resonance. However, if the general characteristics of nuclear magnetic resonance are to be described and related to applications of chemical interest, a full-length review is required, and this is such an attempt. As to the other branches of radiofrequency spectroscopy, excellent reviews of paramagnetic resonance have been given recently by Bleaney & Stevens (2, 3). The book on microwave spectroscopy by Gordy, Smith & Trambarulo (4) contains a chapter on paramagnetic resonance. Discussions of ferro- and antiferro-magnetic resonance are included in the published proceedings of the Washington Conference on Magnetism (5) and the International Conference on Spectroscopy at Radiofrequencies (6).

Introduction

About 400 articles have been published on nuclear magnetic resonance since its discovery in 1946 and more than half are related to problems in the structure of matter. The fundamental character and practical value of nuclear magnetic resonance was recognized by the 1952 Nobel Prize award in physics to the co-discoverers, Felix Bloch and E. M. Purcell. The award addresses are fascinating accounts of the early history of the field. Bloch (7) emphasizes the intimate relation of nuclear magnetic resonance to the Zeeman effect in optical spectroscopy, while Purcell (8) describes the application of nuclear magnetism to structural determinations. Purcell wrote a similar article five years earlier (9), and a comparison of the two articles outlines the rapid growth of such applications. Before discussing the applications, a short description of the basic phenomenon may be helpful.

Nuclear magnetic moments may be pictured as arising from a circulation

[1] The survey of literature pertaining to this review was concluded in January, 1954.

or rotation of the nuclear charge. But mass is associated with the charge, so angular momentum is also present, co-linear with the magnetic moment. If this "spinning top" is placed in an external magnetic field, H_0, the field exerts a torque upon the nuclear magnet, inducing Larmor precession of the spin axis about H_0. A direction in space is defined by H_0, requiring quantization of the nuclear angular momentum in that direction. This establishes a set of $2I+1$ different orientations and Zeeman energies of the nucleus. The frequency separation of the energy levels equals the Larmor precession frequency, $g\mu_n H_0/h$, where g is the ratio of the nuclear magnetic moment μ to the nuclear spin I, μ_n is the nuclear magneton, and h is Planck's constant. Detailed analyses of the spinning nucleus in a magnetic field have been presented by Archibald (10) and Wangsness (11).

Transitions among the magnetic energy levels are induced by a small oscillating field H_1 applied to the sample in a radiofrequency coil perpendicular to H_0. When the radiofrequency equals that of the nuclear Larmor precession about H_0, resonance absorption occurs; it is equivalent to H_1 tilting or nutating the nuclear magnet with respect to H_0, changing the nuclear orientation and energy. This classical model was originally used by Bloch (12) to describe the macroscopic nuclear magnetization. Wangsness & Bloch (13) have since examined the model in more rigorous detail from a microscopic, statistical viewpoint. Mechanical analogues demonstrating nuclear and paramagnetic resonance have been constructed by Carr & Kikuchi (14) and Verbrugge (15).

The resonance frequencies of most magnetic nuclei are between 0.1 and 40 Mc. for fields from 1,000 to 10,000 gauss. The resonance frequency measured in a magnetic field of known strength gives the nuclear gyromagnetic ratio with high precision. The sign of the magnetic moment is obtained by observing the sense of the Larmor precession using Bloch's induction method (12) as described by Proctor (16); and the nuclear spins can be found from intensity measurements. The nuclear spins and magnetic moments of most of the stable nuclei have been determined, and the results are valuable in nuclear theory. Recent reviews of the methods and results include those of Extermann, Béné & Denis (17), Walchli (18), and Ramsey (19). A convenient wall chart summarizing the nuclear magnetic data is available commercially (20). From the chemist's viewpoint, it is unfortunate that only a moderate fraction of nuclei have the magnetic properties desirable for resonance experiments.

The applications of nuclear magnetism to problems in chemical structure arise from the several finer characteristics of the resonance lines. The chief characteristics are the spin-spin and spin-lattice relaxation times, the widths and shapes of the resonance lines particularly if broad, and the resonance shifts, splittings, and complex line structures associated with the electronic environment of nuclei. Also of fundamental value is the dependence of these characteristics upon conditions such as temperature, pressure, the magnetic field, and composition of the system. An effort has been made in this review

to give at least an indirect index to all research published through 1953 on such applications. Most publications not cited have been included in one of the earlier reviews by Dailey (1), Pake (21), Soutif (22), Gorter (23), Darrow (24), Smith (25), or Ramsey (19). The two articles of Pake (21) remain one of the best introductions available on the fundamentals of nuclear magnetic resonance, even though now somewhat dated. The review by Darrow (24) is an exceptionally clear account of both nuclear and paramagnetic resonance for nonspecialists. Ramsey's book (19) was written originally as a review article for physicists, and a chapter was added later summarizing very well most structural applications. Andrew (26) has a book in preparation which promises to give thorough coverage of both the chemical and physical aspects of nuclear magnetism.

Relaxation Phenomena

Spin-lattice relaxation.—One might expect the atomic electrons to be an effective shield between a nucleus and its surroundings. But if so, how can the nuclear spins be brought into and maintain thermal equilibrium with their environment? When a sample is first placed in a magnetic field, the nuclei are randomly oriented. At thermal equilibrium, there are more nuclei oriented in states of low energy than in high. So, some of the nuclear spins initially in the high energy states must give up energy to the other degrees of freedom in the system, i.e., to the "lattice." This cooling process occurs exponentially with a time constant T_1, the spin-lattice relaxation time, which is characteristic of the sample and ranges from 10^{-4} to 10^{4} sec. for different materials and conditions. The value of T_1 is important in the detection of nuclear resonance because a net absorption can occur only if there is an excess of nuclei in the lower energy states. A magnetic field oscillating at the Larmor frequency is required to change the orientation and energy of a nuclear spin. So, if energy transfer occurs between nuclei and lattice, the thermal motions of the lattice must produce such oscillating fields at the nuclei. Therefore, experimental values of T_1 can be combined with a theory for the relaxation process to provide an insight into the thermal motions of the lattice.

Ionic crystals.—Purcell (8) has remarked that our understanding of nuclear relaxation is good in many but not all physical systems. One case still giving some trouble is that of diamagnetic ionic crystals. Local magnetic fields arise from the nuclear magnetic moments themselves. These local fields depend on the internuclear distances, so lattice vibrations produce fluctuations in the local fields and induce spin-lattice relaxation. However, the T_1 values predicted for this model are several orders of magnitude longer than the typical experimental results of Hatton & Rollin (27) and Bloembergen (28). The electronic magnetic moment is a thousandfold larger than the nuclear moments and it is correspondingly more efficient at relaxation. So, it is reasonable that in some cases paramagnetic impurities may play a predominant role in the relaxation, as suggested by Hatton & Rollin (27),

Pound (29), and Khutsishvili (30). Bloembergen (28) verified this experimentally by measuring T_1 in the presence of known concentrations of paramagnetic ions; his theoretical analysis includes spin diffusion effects.

Pound (31) proposed a second mechanism which applies to some types of crystalline solids. Nuclei with $I > \frac{1}{2}$ have electric quadrupole moments, and gradients in the electric field at such a nucleus influence its orientation and energy. For these nuclei, fluctuations in the charge distribution of the lattice can be much more effective at nuclear relaxation than the magnetic effects also present. However, Muto & Watanabe (32) suggest that the two theories apply only to special cases. They are developing a theory considering magnetic interactions between nuclei and the electrons in the filled crystalline band, while in turn, the electrons are coupled to the lattice vibrations.

Group reorientations in solids.—The rotation or reorientation of a structural group displaces the nuclei much more than the lattice vibrations considered above. The oscillations of the local nuclear magnetic fields are proportionately larger, the predicted T_1 values are shorter, and here theory and experiment are in general accord. In fact, the temperature dependence of T_1 can give very useful information about low frequency molecular reorientations, and phase transitions. According to the theory of Bloembergen, Purcell & Pound (33), if the relaxation is produced by one type of reorientation, say rotation of a group about a particular axis, then T_1 is calculated with an equation of the form

$$1/T_1 = K[\tau_c/(1 + 4\pi^2\nu^2\tau_c^2) + 2\tau_c/(1 + 16\pi^2\nu^2\tau_c^2)] \qquad 1.$$

where ν is the resonance frequency, τ_c is the time required for the reorientation, and K is a constant which can be calculated from a structural model for the thermal motions. By means of Equation 1, τ_c can be obtained as a function of temperature from T_1 data. Often an activation energy, E_a, for the reorientations can be estimated by fitting the results to the equation

$$\tau_c = \tau_0 \exp.\ (E_a/RT). \qquad 2.$$

A discontinuity in τ_c indicates a cooperative change or transition in the motions of the groups.

One of the most successful applications of this nature is the work of Sachs, Turner & Purcell (34, 35) on the reorientation of the NH_4^+ ion in the ammonium halides. The proton T_1 changes uniformly with temperature through the λ-point, proving there is no significant change in the motions of the NH_4^+ ion at the transition. Cooke & Drain (36) obtained similar, less complete results; they also investigated methanol, finding a transition in the proton T_1 at the λ-point of the solid. Thomas, Torrey & Alpert (37) measured T_1 in solid methane, and Tomita (38) has proposed a dynamical theory agreeing substantially with experiment. Andrew & Eades have investigated proton relaxation in solid benzene (39) and cyclohexane (40). They conclude that the benzene molecules reorient about their hexad axes against a potential barrier of 3.7 ±0.2 kcal. while in cyclohexane there is a

much larger barrier, 11 ± 1 kcal., hindering reorientation about the triad axis. Wilson & Pake (41) suggest that their data on polyethylene and teflon indicate the co-existence of two phases, one amorphous and the other crystalline.

Liquids and gases.—The Bloembergen, Purcell & Pound theory (33) gives generally satisfactory results for T_1 in liquids; it includes a statistical analysis of the effects of the random Brownian motions. The reduction of T_1 in liquids by paramagnetic ions has often been used to enhance the intensity of weak resonances (7, 33). In principle, the effective magnetic moment, μ_{eff}, of a paramagnetic ion can be calculated from its effect on T_1. However, if the ion forms complexes, the apparent value of μ_{eff} is concentration dependent, as found by Conger (42) and Zimmerman (43). Such phenomena are of potential value in solution chemistry. Research on gases has been discouraged by the weak resonances, but with improved instrumentation considerable information on collision processes should become obtainable. The collision processes in H_2 were analyzed by Bloembergen, Purcell & Pound (33) who predicted an increase in T_1 with pressure. This was verified by their experiments and the later work of Packard & Weaver (44). The reverse applies to He^3; T_1 decreases with increasing pressure but is so long at moderate pressures that Anderson (45) added O_2 as a paramagnetic catalyst to shorten T_1. Bloch (46) has treated nuclear relaxation of He^3 by collision with a paramagnetic solid.

Metals.—In metals the T_1 values are among the shortest observed; most of the data summarized by McGarvey (47) fall between 10^{-2} and 10^{-4} sec. The results are in good agreement with the Heitler-Teller-Korringa theory (48) for the relaxation mechanism; the conduction electrons near the top of the Fermi band are effectively unpaired and interact strongly with the nuclear moments, giving a short T_1. Precise measurements of T_1 in the alkali metals by Holcomb & Norberg (49) suggest there are also nuclear quadrupole interactions with lattice imperfections. Hydrogen absorbed in palladium was investigated by Norberg (50) who found proton-conduction electron interactions and diffusion of protons in the metal. Torrey (51) has developed a detailed theory for spin-lattice relaxation by diffusion.

Spin-spin relaxation.—Besides interacting with the lattice, the nuclear magnets interact among themselves, producing spin-spin relaxation with a characteristic time T_2. The local fields from magnetic neighbors have, in general, a static and an oscillating component both of which contribute to the T_2 of a nucleus. The static components add to or subtract from the externally applied field so the total fields at different nuclei may vary by several gauss and the resonance is broadened or split correspondingly. The oscillating components produce spin exchange; if two neighboring nuclei are antiparallel, but precessing at the same frequency, the oscillating field from each can flip the other over, interchanging their energy. Both processes disrupt the phase relations of the precessing nuclei, the static fields because they cause differences in the precession frequency, and the spin exchange because the phase

relations are interchanged. Accordingly, Hahn (52, 53) has called T_2 the spin phase memory time. Also, the magnetization perpendicular to H_0 is governed by the phase relations of the precessing nuclei, so Bloch (12) calls T_2 the transverse relaxation time. It should be noted that spin-lattice relaxation also contributes to T_2.

Transient effects are associated with T_2. When the resonance condition is swept through rapidly, damped oscillations are observed in the tail of the resonance. These "wiggles" were first explained by Purcell (33) who pointed out that they occur when the nuclear magnetization hasn't time to follow the changing applied fields through resonance. A transverse magnetic moment remains; it precesses about H_0, induces a signal at the precession frequency, and decays with the time constant T_2. After resonance, the precession frequency differs from the applied radiofrequency, and the beats between them appear as the damped oscillations. Jacobsohn & Wangsness (54) have developed a full account based on Bloch's equations (12). Verification and elaboration of various experimental and theoretical details have been given by a number of workers, including Giulotto & Chiarotti (55, 56), Extermann, Denis & Béné (57, 58), Strick *et al.* (59), Bhar & Bhar (60), and Ayant (61). Gvozdover & Magazanik (62) express the form of the signals in integral equations of the Volterra type, while Gabillard (63) has used a Fourier expression to integrate Bloch's equations. Eisenstein (64) has treated spin-spin relaxation in a system of two particles of spin $\frac{1}{2}$. The line-broadening aspects of T_2 are included in the following section.

Absorption Line Shapes and Widths

The nuclear environment influences the width and shape of a resonance line, so these details can provide information about the structure of a system. We will neglect artificial broadening by field inhomogeneities or by saturation effects resulting from applying too intense a radiofrequency field; these can be minimized experimentally. Electric quadrupole interactions of nuclei with $I > \frac{1}{2}$ are discussed in a later section. Probably the commonest broadening is that provided by the relaxation processes mentioned above.

T_1 broadening.—If the lifetime of a nuclear spin state is T_1, then by the Heisenberg uncertainty principle there is a spread in the energy given by $T_1 \Delta E = h/2\pi$. The resonance line is broadened appreciably (>0.01 gauss) if T_1 is the order of 10^{-3} sec. or less. This type of broadening has been observed in solutions of paramagnetic ions (33) and in metals (47). Theoretically, a Lorentzian line shape is predicted when the width arises primarily from T_1, and McGarvey (47) found this to be so in his experiments with metals. In such cases the line width is a convenient measure of T_1.

T_2 broadening in rigid lattices.—The interaction of two nuclear spins, encountered in the discussion of T_2, is of the form (33)

$$\mathcal{H} = [\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 - 3(\boldsymbol{\mu}_1 \cdot \mathbf{r})(\boldsymbol{\mu}_2 \cdot \mathbf{r})r^{-2}]r^{-3}, \qquad 3.$$

where $\mathbf{r}$ is the vector joining nucleus 1 to nucleus 2. The first term represents

the static components of the local fields, and the second term the precessing components. However, the orientation of $\mathbf{r}$ with respect to H_0 influences the magnitude and sign of the interactions, so if the nuclei are in motion, the effects tend to cancel out. At present we will assume such motions to be absent and consider the structural information obtainable from the resonance line shapes and widths in "rigid lattices."

The two-spin system.—The simplest case is that of two like spins, with $I=\frac{1}{2}$, occurring as isolated pairs in a single crystal. Pake's solution (65) gives the complete line shape, which is split into two equal components separated by $3\mu\mu_n r^{-3}|3\cos^2\theta-1|$, where θ is the angle between $\mathbf{r}$ and H_0. The proton resonance observed by Pake in a single crystal of gypsum, $CaSO_4\cdot 2H_2O$, agrees with the theory when allowance is made for the small broadening effects of magnetic neighbors outside each proton pair. Moreover, the splitting which varies between 0 and 22 gauss gives a value, 1.58 Å, for the proton-proton distance in the H_2O molecules; the H_2O orientations in the crystal are determined from the angular dependence of the splitting. If the crystal powder is used, the resonance line shape is that computed by averaging the angular dependence over a sphere. The average line shape retains two components but they are broadened and give a less accurate proton-proton distance. This general method of structural determination has its greatest usefulness for hydrogen which is difficult to locate with x-rays because of its small scattering but which has excellent magnetic resonance characteristics.

Methods analogous to those of Pake (65) have been used by Itoh and his co-workers (66 to 69) on several other single crystal hydrates. In $K_2CuCl_4\cdot 2H_2O$ they found (66) the H—H distance to be 1.62 Å and the proton pairs directed along the [110] and [1$\bar{1}$0] directions. $(NH_4)_2CuCl_4\cdot 2H_2O$ has a similar structure while in $CuCl_2\cdot 2H_2O$ the proton pairs are at angles $\pm 37.5°$ to the *a*-axis in a plane perpendicular to the *b*-axis. The water molecules in $K_2HgCl_4\cdot H_2O$ and $K_2SnCl_4\cdot H_2O$ (67, 68) are themselves distributed in the lattice as pairs, separated by 3.60 and 3.90 Å, respectively, in the two compounds. The interactions between the two two-spin systems are appreciable, giving a more complicated resonance, which has nonetheless been analyzed in detail (69).

The three-spin system.—Andrew & Bersohn (70) calculated the line shape for three like spins, with $I=\frac{1}{2}$, at the corners of an equilateral triangle. A nine-component resonance is predicted for the isolated group; in crystal powders the fine structure averages to a three peak line. The protons in a CH_3 group are a common three-spin system; and Purcell *et al.* (71) found the proton resonance in CH_3—CCl_3 to agree substantially with theory at temperatures low enough to give a rigid lattice. Powles (72) has investigated several tetra-substituted methanes containing CH_3 groups and calculated the effects of various amounts of external broadening upon the three-spin line shape. Proton resonance data have established the existence and structure of the hydronium ion, H_3O^+, in several solids; Smith (25) has reviewed the details of this important application.

A rather different three-spin system, the linear ion $(FHF)^-$, was investigated theoretically and experimentally by Waugh, Humphrey & Yost (73). The problem here is fundamental to hydrogen bonding; it is to determine whether the proton is in a single or a double potential minimum between the two fluorines. The predicted fluorine resonance in the crystal powder KHF_2 is double while the proton resonance is triple. The observed data, combined with x-ray positions for the K and F, confirm the symmetrical structure for $(FHF)^-$, the proton lying within ± 0.06 Å of the ion center.

Second moments of N-spin systems.—The complexity of the line shape increases rapidly with the number of interacting spins and at the same time the details are obscured by broadening from magnetic nuclei outside the primary group. For example, Bersohn (74) calculated the spectrum of a tetrahedral four-spin group such as the protons in NH_4^+; Tomita (38) made a similar partial analysis for CH_4. The calculations predict from 7 to 20 lines depending upon orientation of the tetrahedron, but the proton resonance observed in the ammonium halide powders (36, 71, 74) is simply very broad and flat topped. Fortunately, as shown by Van Vleck (75) and also by Pryce & Stevens (76) the moments of an absorption line can be computed theoretically for a given structural model. And often this theoretical second moment ΔH_2^2 is as valuable for comparison with experiment as is the line shape. Van Vleck's result (75) may be written (71) as

$$\Delta H_2^2 = (3/2)I(I+1)N^{-1}g^2\mu_n^2 \sum_{j>k} (3\cos^2\theta_{jk} - 1)^2 r_{jk}^{-6} + (1/3)N^{-1}\mu_n^2 \sum_{j,f} I_f(I_f+1)g_f^2(3\cos^2\theta_{jf} - 1)^2 r_{jf}^{-6}. \quad 4.$$

N is the number of nuclei at resonance over which the calculation extends, while the subscripts f refer to other magnetic species. Second moment considerations were useful adjuncts to most of the line shape studies outlined above. In a crystal powder the angular dependence averages to 4/5 and the computation reduces to the r^{-6} summation.

The second moment of a crystal powder can give, in principle, only one structural parameter and this requires that the broadening be particularly sensitive to that one parameter. The latter condition is not too severe because the second moment depends upon r^{-6} and most broadening is from nearest neighbors. In the ammonium halides 9/10 of the broadening is from interactions within the NH_4^+ ion, and second moment studies (36, 71, 74) yield a value of 1.035 ± 0.01 Å for the N–H distance. Similarly, Pratt & Richards (77) demonstrated the existence of the ion $N_2H_6^{++}$ in the hydrazine salts $N_2H_6(NO_3)_2$ and $N_2H_6C_2O_4$, and determined the H–H distance to be 1.71 ± 0.015 Å. Other cases include urea, for which Andrew & Hyndman (78) have obtained some evidence of a planar structure, and glycine for which Shaw *et al.* (79) suggest the zwitterion configuration, $H_3N^+CH_2CO_2^-$. For benzene, Andrew & Eades (39, 80) devised an ingenious method of isotopic substitution to obtain a value of 2.495 ± 0.018 Å for the separation of adjacent protons. Deuterium has a small magnetic moment so in C_6H_5D and 1,3,5-

$D_3C_6H_3$ the proton second moments are smaller than in C_6H_3. Three independent equations such as Equation 4 are obtained, separating the inter- and intra-molecular broadening, and giving the desired distance.

In general, the most information is obtained by combining line shape, second moment, and angular dependence studies of single crystals. Relatively large crystals (1 cm.^{3}) are required but the more detailed conclusions warrant the trouble. Thus, Itoh *et al.* (81) were able to show that $(COOH)_2 \cdot 2H_2O$ did not contain H_3O^+ ions; they determined the positions of all the protons, using a single crystal. This type of complete, single crystal study has also been made by Soutif (82) of $LiSO_4 \cdot H_2O$ and by Bersohn *et al.* (74) of NH_4Cl. In the latter, the N–H distance was obtained more accurately than with data from the crystal powder. Also, it was shown that the tetrahedral NH_4^+ ions are oriented with the N–H bonds pointing towards the unit cube corners, and the order-disorder nature of the λ-point was confirmed.

Some attention has been given to possible sources of error in such structure determinations. Perlman & Bloom (83) and Andrew (84) have considered the artificial broadening of an absorption line by the magnetic field modulation ordinarily used in plotting the line shapes. Andrew's more rigorous result is that the apparent experimental second moment is larger than the true value by (1/4) H_m^2, where H_m is the modulation amplitude. Except for very weak absorption, H_m can be kept low enough to produce a negligible effect. Burgess & Brown (85) have discussed the perturbing effect of the modulation frequency; this too is ordinarily negligible. The zero-point oscillations of protons are more serious; they can produce a significant narrowing of an absorption line from that of a rigid lattice by the mechanism discussed in the next section. Bersohn (74) found the effect to reduce the second moment in the ammonium halides by nearly 10 per cent from the rigid lattice value.

Molecular motions and the temperature dependence of line shapes and widths. —If the lattice is not rigid, the angular factors $(3\cos^2\theta - 1)$ in Equation 4 must be averaged in time. If the motion is fast and random, the factors average to zero and the resonance line is narrow (<0.01 gauss). Bloembergen, Purcell & Pound (33) have analyzed the narrowing process in terms of the correlation time τ_c, which is the average time required for a reorientation of the group containing the interacting nuclear spins. Line narrowing occurs when ν_c, defined as $(2\pi\tau_c)^{-1}$, is comparable to the frequency width $\delta\nu$ of the resonance. Their result may be written (86) as

$$(\delta\nu)^2 = A^2(2/\pi)\tan^{-1}[\alpha(\delta\nu/\nu_c)], \qquad 5.$$

where A is the rigid-lattice line width and the factor α is the order of unity, depending upon the line shape. In typical systems A is between 10 and 100 kc., so motions in this frequency range can be detected by line width measurements. In an early application of this sort, Alpert (87) observed the temperature dependence of the proton resonance in several molecular solids exhibiting phase transitions. The absence of any significant changes in line

width at the transition temperature in most cases eliminated the onset of free molecular rotation as the transition mechanism.

The existence of hindered rotational motions can be inferred from quantitative studies of line shapes and second moments. Particularly simple examples are the two-spin and triangular three-spin systems restricted to rotation about an axis perpendicular to a plane containing the nuclei; this motion reduces the line shape to only 1/2 and ΔH_2^2 to 1/4 the rigid lattice values. These theoretical results were obtained by Pake (86) and Andrew & Bersohn (70) who computed the appropriate time averages of the angular factors in Equations 3 and 4. Actual systems showing such behavior have been observed. A two-spin case (86) is 1,2-dichloroethane which starts rotating about the long molecular axis at a temperature coinciding with a heat capacity anomaly and change in crystal form. CH_3 groups restricted to rotation about their C_3 axes were found in a number of compounds (86). Powles (72) has determined that such CH_3 group motions occur in all of several tetrasubstituted methanes at temperatures above $-160°C$. Further line narrowing at higher temperatures results when the carbon skeleton of the molecules starts reorienting; and this motion is more sensitive to the size and shape of the molecule. Powles' results (88) on solid solutions of *t*-butyl chloride in CCl_4 confirm, in general, the phase diagram suggested by thermal and dielectric measurements. Also, the freedom of the CH_3 groups to reorient depends upon inter- as well as intra-molecular forces. A very striking case of rotational hindrance was discovered by Spence and his co-workers (89, 90); the proton line shape in the liquid crystal phase of *p*-azoxyanisole suggests that the molecules are there restricted to rotation about the long molecular axis.

Other diverse research has been reported. Andrew (91) investigated four long chain aliphatic and eight aromatic hydrocarbons. The aliphatic compounds are dimorphous, and it was concluded that molecular rotation occurs in the high temperature form. Similar behavior has been observed by Kojima & Ogawa (92) in cetyl alcohol. Andrew also made a theoretical analysis of the effect of rotational oscillations upon the second moment. He suggested that several of the aromatic compounds rotate in the solid; however, Rushworth (93) has pointed out that impurities gave misleading results in anthracene. Proton resonance techniques are being used to investigate the unusual physical properties of silicone polymers. Rochow has obtained preliminary results [Leclair, Sternberg & Rochow (94)] on several methyl polysiloxanes, which suggest an unusual freedom of motion not only of the methyl groups but of the heavy atom skeleton. Meyer (95) has observed the temperature dependence of the proton line widths in natural rubber. A change in width at about $-120°C$. is assigned to CH_3 group rotation, while a larger change at $-50°C$. is assigned to segmental motions. It is interesting to note that the latter change coincides with the second order transitions and confirms their cause. Earlier work on polymers was reviewed by Dailey (1). Garstens (96, 97) has compared the proton resonance widths of hydrogen absorbed in Ta and Ti with the widths in metallic hydrides; the narrow lines found in Ta indicate the protons there are relatively free.

The proton resonance in solid H_2 has some very interesting features. Hatton & Rollin (27) made the first low temperature observations which presented several anomalies, later discussed by Tomita & Mannari (98). Recently, Reif & Purcell (99) completed a detailed experimental and theoretical study of the line shapes and their change with temperature. The proton resonance arises only from the *ortho* molecules which are in the ordinarily threefold degenerate rotational state $J=1$. The line shapes observed are accounted for quantitatively by the effect of the rotation upon the local magnetic fields and by the lifting of the degeneracy by the crystalline potential. An intriguing outgrowth of the experiments was the detection of the proton resonance with zero applied field; the resonance frequency of 165 kc. corresponds to the local field within the H_2 molecules.

The resonance line widths undergo large fractional changes over only a small range of reorientation frequencies. This and the uncertainty in α, the line shape parameter, make line width changes and Equation 5 not very satisfactory for determining the reorientation frequency as a function of temperature. However, this has been done in several cases, such as the metals where self-diffusion narrows the resonance (47). Activation energies were then evaluated for the reorientation process by applying Equation 2. In the discussion of relaxation processes, Equation 1 related τ_c (and thereby ν_c) to T_1 and T_1 values can be measured over several decades. So, the best procedure is to combine T_1 and line shape data. The line shape changes identify the type of reorientation and the T_1 data can give accurate values of the activation energy. Several of the researches discussed in one connection or the other actually incorporated both types of data (36, 39, 40, 50, 74). Possible applications of this sort are extensive.

Electronic Effects in Nuclear Resonance

Chemical shifts.—An important method of structural analysis by nuclear resonance arises because the magnetic field at a nucleus is in general not the same as that in the bulk sample. Small but significant differences are produced by interactions between the applied magnetic field and the motions of the electrons in the sample. The effect can be represented as $H_0=H_b(1+\sigma)$, where H_0 is the net field at the nucleus; H_b, that applied to the bulk sample; and σ is an "internal magnetic susceptibility" of the electron distribution. Usually σ is negative, corresponding to an internal diamagnetism or magnetic shielding of the nucleus. In different compounds the differences in the electron distribution about a nucleus give different values of σ, producing a "chemical shift" in the location of the resonance. Complex resonance lines occur in samples with structurally nonequivalent sites. Most resonance shifts have been measured at a fixed resonance frequency as $\delta=(H_r-H_c)/H_r$, where H_r is the magnetic field applied for resonance in an arbitrary reference compound and H_c is that for the compound in question. The sign convention for δ is reversed from σ.

Chemical shifts were discovered by Knight (100) who found that the phosphorus resonance position varied by about 0.01 per cent in several

compounds. Similar effects were found independently by Dickinson (101) in fluorine and phosphorus compounds and by Proctor & Yu (102) in nitrogen. The shifts are often small, requiring narrow lines and thus liquid or gaseous samples for the measurements. A general theory applicable to molecules has been developed by Ramsey (103). The theory is formally similar to the treatment of the bulk magnetic susceptibility, except that the effect is calculated at a nucleus. There is a diamagnetic term which can be related to the electrostatic potential at the nucleus. Only this term is present in atoms and ions, where it is proportional to $Z^{4/3}$; values computed by Dickinson (104) from Hartree functions range from -1.8×10^{-5} for $Z=1$ to -1.16×10^{-2} for $Z=92$. In molecules there is a second-order paramagnetic term with a magnitude comparable to but opposing the diamagnetic. This paramagnetic term is difficult to evaluate and complete calculations have been made only for H_2. The chemical shifts are independent of temperature in most cases.

Hoffman (105) made a systematic study of the fluorine and proton resonance shifts in many of the binary covalent fluorides and hydrides. The results for the fluorides are the simplest. F_2 has the least shielding, 6.3×10^{-4} less than in HF; and between these extremes the fluorine shifts are proportional to the electronegativity of the atom bonded to the fluorine. Recently, Saika & Slichter (106) completed an encouraging analysis of these results, developing a simplified version of Ramsey's theory. In their model, the resonance shift between F_2 and F^- is attributed solely to polarization by the applied field of the large orbital magnetic fields in F_2, produced by the instantaneous imbalance of the p electrons in the valence shell of a given fluorine. For a bond with partial ionic character i, the fluorine resonance will occur at an approximate fraction $(1-i)$ of the shift between F_2 and F^-. HF with 43 per cent ionic character is calculated to be shielded 14×10^{-4} more than F_2, which agrees reasonably well with the experimental value, 6.3×10^{-4}. Moreover, the ionic character of a bond is proportional to the electronegativity difference of the bonded atoms, which explains the observed similar dependence of the fluorine shifts. These calculations neglect any differences in the diamagnetic term. For hydrogen this approximation wouldn't be as good, and, in fact, the observed proton shifts exhibit more complex trends than the fluorine shifts.

Shifts of the fluorine resonance in substituted fluorobenzenes were observed by McCall, McGarvey & Meyer (107). The results are correlated with the effect of the substituent upon the electron distribution in the benzene ring and demonstrate the existence of different interaction mechanisms at the *meta* and *para* positions. Also, the electronic effects of the substituents were shown to be additive in most polysubstituted benzenes. Meyer (108) measured both the fluorine and proton resonance shifts in many of the halomethanes, obtaining qualitative arguments for the relative importance of ionic and double bond structures. The proton shifts in simple organic groups were found by Meyer & Saika (109) to agree in general with accepted con-

cepts of electronic structure. For example, the proton in the OH group shows progressively less shielding and therefore increasing ionic character in alcohols, phenols, and acids, in accord with their increasing acidity. Shoolery (110) noted a similar correlation between the proton shifts of the CH_2 group in subsituted ethanes and the electronegativity of the substituent. Brother Peter (111) has measured phosphorus shifts in a large number of compounds and analyzed the results in terms of additive partial shifts for each atom bonded to the phosphorus. Phosphorus shifts have also been reported by McCall (112), who gives an intercomparison of proton, fluorine and phosphorus shifts and suggests that all three correspond qualitatively to changes in "electron density" about the nuclei.

The chemical shift data for other nuclei are generally insufficient for any detailed conclusions about electronic structure. Dickinson (101) included some shifts on boron compounds. Lindström (113) has remarked upon the unusually large fluorine shifts in fluorocarbons. The chemical shifts published prior to April, 1953 are summarized in Walchli's table (18). A recent promising result is that of McGarvey (114), who found the Rb^{87} and Cs^{133} resonances to be shifted by sizeable amounts in the different solid halides. These shifts must be associated with distortion of the ions from spherical symmetry; and a detailed interpretation of the shifts might contribute to our understanding of the crystalline electronic structure.

Besides their theoretical significance, the chemical shifts can be very useful in determining molecular structures. The general appearance of the resonance in a liquid sample is predicted directly by the number and relative populations of nonequivalent sites for the nucleus in the structure postulated. Thus, Hoffman (105) proved that BrF_5 and IF_5 have tetragonal pyramid structures simply by resolving the fluorine resonances in the liquid samples into two components, with relative intensities of 4:1. Another example is the resolution by Arnold, Dharmatti & Packard (115) of the proton resonance in ethanol into three components; the relative intensities of 3:2:1 identify the protons in the CH_3, CH_2, and OH groups. The proton shifts in simple organic groups are characteristic of the group (109); and the overlapping of different groups is rather small. Moreover, the effects of adjacent groups in the same molecule are themselves sufficiently characteristic to be a further aid in structural analysis.

A typical application is the measurement of the keto-enol tautomerism in acetylacetone by Meyer (116) and Jarrett, Sadler, & Shoolery (117). The proton shifts in a number of boranes have been reported by Kelly, Ray & Ogg (118); the results confirm the bridge structures and give a measure of the differences between bridge and terminal bonds. Fluorocarbon chemistry is a favorable field for this method. Shoolery (119) has surveyed several types of fluorocarbons and characterized the resonance shifts, while Tiers *et al.* (120) have applied the results to the structural analysis of 1,1,di-H perfluoroalkyl halides.

Chemical exchange and solutions.—If there is fast exchange of nuclei

among different chemical species, then the electronic environment and chemical shift is averaged and a single resonance line occurs rather than a separate line for each species. The averaging process is influenced by concentration and temperature so these parameters should produce changes in the chemical shift. Such phenomena were described by Arnold & Packard (121) for ethanol, in which the proton shift of the OH group depends on temperature and on the concentration in CCl_4. Liddel & Ramsey (122) suggested the effects probably result from association of the hydroxyl groups by hydrogen bonding. Saika (123) observed concentration dependent proton shifts in aqueous solutions of several proton-containing electrolytes. The data demonstrate the incomplete dissociation of HNO_3, H_2SO_4, $HClO_4$, and NaOH in concentrated solutions.

Masuda & Kanda (124) arrived at similar conclusions from the concentration dependence of the N^{14} resonance in nitric acid solutions and from the halide resonances in HCl, HBr, and HI solutions (125). McGarvey (126) has reported the linear variation of the Tl^{+1} and Tl^{+3} resonance positions with anion concentration, suggesting the importance of some imperfectly understood interionic effects. It would seem that new information can be obtained on the structure of solutions and liquids by studying these phenomena. Moreover, Saika's analysis (123) shows that exchange will average an otherwise complex resonance to a single line if the lifetimes of the different chemical species are less than a determinable value, between 10^{-2} and 10^{-4} sec. In this way, rapid exchange rates might be measured, which would be a very significant application.

Electron coupled spin-spin interactions.—Complex resonance lines have been resolved in many instances to show fine structure not accounted for by chemical shifts. An early case was PF_3 in which Hoffman (105) found the fluorine resonance to be a symmetrical doublet and McCall & Slichter (127) later found the phosphorus resonance to be a quartet with relative intensities of 1:2:2:1. The Sb^{121} and Sb^{123} resonances in aqueous $NaSbF_6$ were observed by Proctor & Yu (128) to have an unusual structure, with seven components, confirmed by Dharmatti & Weaver (129). Hahn (52) discovered a "slow-beat" phenomenon in his spin-echo experiments and this was shown subsequently by McNeil & Slichter (130) and Hahn & Maxwell (131) to correspond to the multiplet resonances resolved directly in the steady-state experiments. This fine structure is independent of the temperature and applied magnetic field; and splittings have been observed from 10^{-3} to 2 gauss. The effect results from a coupling of nonequivalent sets of magnetic nuclei by the bonding electrons. The number of components in the resonance of one set equals $2M_I+1$ where M_I is the total spin of the nuclei in the other set. The relative intensities of the components equal the statistical weights of the different spin combinations m_I. A combination of chemical shifts and "multiplet interactions" can lead to rather complex spectra, particularly when the two effects are of comparable magnitude, as pointed out by Hahn & Maxwell (131).

The predominant interaction is the magnetic coupling of each nucleus with the spin of its electron and the exchange coupling of the electron spins in the covalent bond, as pointed out by Ramsey & Purcell (132). Calculations made by Ramsey (133) on HD are in reasonable agreement with the coupling energy of 43.5 ±1 cps. found by Carr & Purcell (134) and 42.7 ±0.7 cps. by Wimett (135). The magnitude of the coupling is governed by the bonding wave functions, and it seems likely that valid inferences about bond character can be drawn from observed splittings, as attempted by McCall & Slichter (127). Also, the splitting is greatest between directly bonded nuclei, and the presence or absence of splitting can be useful information. For example, the phosphorus resonance in H_3PO_3 is a doublet, which indicates that only one proton is attached directly to the phosphorus; and the triplet phosphorus resonance in H_3PO_2 shows that two protons are bonded to the phosphorus. Chemical exchange averages out the splitting (127) as well as the resonance shifts, and Ogg (136) has suggested that the occurrence of the splitting offers an operational criterion of covalent bonding. Not all aspects of the splittings are understood. Quinn & Brown (137) report that the fluorine splitting in $(HO)POF_2$ disappears at fields below 500 gauss, and no satisfactory explanation has been proposed. Other effects will no doubt be discovered.

Conduction electron shifts in metals.—In metals the resonance position occurs at considerably lower applied fields than in compounds. This "Knight shift" (100) results from the paramagnetism of the conduction electrons, as suggested by Townes, Herring & Knight (138), and is a much more sensitive measure of the electronic paramagnetism than the bulk susceptibility. The considerable number of shifts measured are summarized by Walchli (18) and McGarvey (47). The resonance shifts and the spin-lattice relaxation time T_1 are interdependent in metals as shown theoretically by Korringa (48) since both depend upon the density of the conduction electron wave functions near the nucleus. In turn, McGarvey (47) related the resonance shifts to the T_1 broadening of the resonance lines. The resonance shifts were measured by McGarvey (139) in several metals over temperature ranges of 200° including the melting point, and changes of no more than five per cent were found. These small effects arise from the volume dependence of the mass magnetic susceptibility and of the wave functions for the conduction electrons. The various phenomena afford sensitive checks on the validity of wave functions proposed for the conduction electrons. Detailed calculations of this sort have been attempted for lithium by Kohn & Bloembergen (140). Another type of application was made by Knight & Kittel (141) who used the resonance shifts as evidence against antiferromagnetic electronic structures for some of the transition elements.

The effects of paramagnetic ions.—The reduction of T_1 by paramagnetic ions was mentioned earlier. In addition, Dickinson (101) discovered that paramagnetic ions in solutions produce a concentration dependent nuclear resonance shift. Grivet & Ayant (142) later made similar observations. One

might expect that the thermal motions in a liquid would average out the local fields associated with the paramagnetic ions, giving no net shift but simply a T_1 broadening. However, Bloembergen & Dickinson (143) and Grivet & Ayant (142) have developed theories which include anisotropic factors. Relatively little has been done on the problem, but it should yield information of value regarding ionic solvation and interaction processes.

The local magnetic fields associated with paramagnetic ions are enormous compared to those from magnetic nuclei, so very large splittings of the nuclear resonance can be expected in rigid lattice paramagnetic samples. Bloembergen, Poulis & Hardeman (144, 145, 146) have made several studies of such splittings of the fluorine and proton resonances in single crystals of the antiferromagnetic materials MnF_2, $CuSO_4 \cdot 5H_2O$, and $CuCl_2 \cdot 2H_2O$. The resonances were observed as a function of temperature, crystal orientation, and applied field, and the results agree well with theory. In $CuCl_2 \cdot 2H_2O$ it was possible (146) to calculate the proton positions. Kambe & Usui (147) have given a general theory for nuclear resonance in paramagnetic crystals.

Quadrupole splitting.—Nuclei with $I > 1/2$ have electric quadrupole moments and if there is an electric field gradient at the nucleus a quadrupole energy term is added to the magnetic energy. The quadrupole energy may be as little as a few kc. or as much as 1000 Mc. depending upon the nucleus and the electric field gradients. In liquids and gases the molecular reorientations tend to average out the field gradients, which then serve mainly as relaxation mechanisms; but if the quadrupole energies are large the averaging may be incomplete or the relaxation so effective that the magnetic resonance is broadened past detection. In rigid lattice solids the quadrupole interactions split the magnetic resonance. Theoretical analyses of various features of the interactions in solids have been made by Pound (31), Bersohn (148), and Volkoff *et al.* (149 to 152). Significant parameters include the relative magnitudes of the quadrupole and magnetic energies, the symmetry of the crystalline and/or molecular electric field gradients, and the orientation of the electric field gradient with respect to the magnetic field. In a single crystal the magnetic resonance is split into $2I$ components, and this has served as a method of spin determination.

The quadrupole energy is given by the product of the quadrupole moment and the field gradient, so if a quadrupole splitting is observed and the quadrupole moment known, the field gradient can be derived. This would seem to be one of the more important uses of the quadrupole splittings. A study of basic interest has been made by Cotts & Knight (153), who found the quadrupole splitting of the Nb^{93} magnetic resonance to be a sensitive indicator of the phase changes undergone by $KNbO_3$. In particular, there is a ferroelectric transition at 435°C., and it is to be hoped that the changes in quadrupole splitting will be of value in studying the mechanism of such transitions. In cubic crystals there should be no field gradients at the nuclei because of the crystal symmetry. However, random fields associated with imperfections and strains in cubic crystals were found by Watkins & Pound (154) to split

and broaden the magnetic resonance so that only the central undisplaced but weakened line is detectable. This effect could serve as a sensitive measure of internal strains. Also, Bersohn (148) has suggested that the temperature dependence of the quadrupole splitting might be used to investigate group reorientations in a manner similar to the magnetic dipolar splitting.

Other Applications

Thomas, Driscoll & Hipple (155) at the U. S. Bureau of Standards determined the proton magnetic moment in absolute units by measuring directly both the proton resonance frequency and the applied magnetic field. A less accurate measurement has since been made by Lindström (113). The results enable the precise determination of a magnetic field simply by observing the proton resonance frequency in it. Instruments for this purpose have been described by Hopkins (156), Knoebel & Hahn (157) and Béné *et al.* (158) among others, and at least two commercial models are available (20, 159). Béné, Denis, and Extermann have used similar techniques for measuring magnetic field gradients (160) and for determining intense D.C. currents (161). Nuclear resonance signals have also been used extensively for regulating electromagnets when high stability is required; a representative system is that described by Thomas (162).

Very little seems to have been done in the way of quantitative analysis by nuclear resonance. Absolute intensity measurements in different samples and for different nuclei are not easy, though they have been made (154, 163). Shaw & Elsken (164, 165, 166) have developed methods for determining the water content of assorted hygroscopic and agricultural materials. "Free water" is readily differentiated from water or protons incorporated in a carbohydrate or protein structure; the free water gives a narrow proton resonance while the bound protons give broad absorption. O'Meara & Rollwitz (167, 168) have successfully extended such determinations to the corn wet-milling industry. In recent work, Elsken & Shaw (169) have designed a sensitive null-balance system for quantitative measurements with improved precision.

Instrumentation

Nuclear magnetic resonance produces relatively weak effects and sensitive instruments are needed for its detection. Six general methods have been invented. The radiofrequency bridge was first used for nuclear resonance by Purcell (33). Several variations have been described (170, 171, 172). An rf oscillator activates the bridge which balances out most of the rf applied to the sample, so that the signals associated with the resonance are a larger fraction of the bridge output. The induction method of Bloch (12, 16) differs from the others in having a separate rf coil to pick up the resonance signals; this coil is perpendicular to both H_0 and the sample coil to which the rf power is applied. The ultimate sensitivity of the various methods would seem to be much the same; however, in their search for weak resonances the Stanford group has most nearly attained the limits. Weaver (173) has de-

scribed a nuclear induction spectrometer which detected H^2 and O^{17} in water at their natural abundance of 0.02 and 0.04 per cent.

Roberts (174) found that a sample in the tank coil of a superregenerative or regenerative oscillator changes the oscillation level and frequency by detectable amounts at nuclear resonance. The superregenerative spectrometer has been used most widely by Williams and his group (175, 176); it has some advantages for nuclei with short T_1 but gives a complex resonance pattern. Pound, Knight & Watkins (177, 178) have designed an excellent regenerative spectrometer; several other circuits of the general type have been published (156, 179, 180, 181). Methods incorporating transient rather than steady state resonance phenomena were invented by Torrey (182, 183) and Hahn (52, 53). In Torrey's method the radiofrequency power is applied as a pulse with H_0 kept constant at or near resonance; and with the rf left on, a decaying beat signal is generated by the nuclear nutations. In Hahn's method, the rf is applied in short intense pulses, and the resonance shows itself as a transient "Bloch decay" trailing each pulse or as separate "spin echoes" induced by the nuclei after two or more applied pulses.

Photographic and magnetic tape recording tricks for integrating noise and detecting weak signals have been proposed by Ross & Johnson (184) and Suryan (185). Also, Suryan (186) observed nuclear resonance in flowing liquids, which can give some improvement in signal and affords a striking demonstration of relaxation effects. The instrumentation requirements for the various resonance phenomena differ widely; the matter has been discussed in part by Meyer & McClure (187). Broad absorption line shapes can be plotted using an induction or regenerative spectrometer or an rf bridge. Usually the first derivative of the resonance is observed by modulating H_0 at some low audiofrequency ($\sim$100 cps.) with an amplitude less than the line width. The resonance signal modulates the rf which is detected, amplified with a narrow-band phase-sensitive amplifier (33, 188) to improve the signal-to-noise ratio, and the output observed on a meter or recorded automatically. The resonance is plotted by changing slowly either H_0 or the radiofrequency. Commercial circuits adaptable for broad line research are available (159).

The resolution of complex resonances in liquids requires field homogeneity over the sample comparable to the natural widths and separations of the components. And for protons, this is the order of milligauss. The design and homogenization of permanent magnets for this purpose have been described (187, 189). Also, special electromagnets with regulated power supplies and high resolution spectrometers are produced commercially (20). High resolution requires the slow-sweep modulation method proposed by Béné, Denis & Extermann (190) to eliminate interference from the relaxation wiggles. The interference produces beat frequencies related to the resonance structure (52, 191, 192) but the analysis is difficult and generally less satisfactory than the direct resolution. Taylor (193) has described an impressive variation of the slow sweep; an electromagnet was swept rapidly over several hundred

gauss, giving oscilloscope display of resonances from different nuclei in the same sample and of resonances widely split by quadrupole interactions.

There are a considerable number and variety of methods for observing relaxation times. T_1 was first measured in saturation experiments (33); the spin system is heated by applying intense rf power, and the cooling off is checked periodically by measuring the absorption from a weak rf field. Short T_1 or T_2 values can be inferred from line widths (33, 47) depending upon which process governs the width. The transient effects are particularly good for T_1 and long T_2 values ($>10^{-3}$ sec.). Hahn's pulse method (52, 53) is very good for both T_1 and T_2, but considerable electronics is required. Various other procedures have been described for T_2 (194, 195, 196) and for T_1 (197, 198).

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CRYSTALLOGRAPHY[1]

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Nearly all writers of reviews on crystallography in recent years have found it necessary to point out that the annual volume of publication is so vast that their articles must inevitably be highly selective. While the selection is normally made in such a fashion that all the most important current trends in the subject are clearly indicated, particular researches of considerable interest may well escape mention, and it may therefore be helpful to start this article by giving some guidance to the reference literature of crystallography for the benefit of the reader who requires something approaching 100 per cent coverage at a reasonably detailed and critical level.

The standard reference work of the pre-x-ray era, still of inestimable value, is the five-volume *Chemische Krystallographie* of Groth (1) in which are critically summarized the morphological and optical data for over 7000 crystalline substances. Groth's contemporary, E. S. Federov, conceived the idea of using morphological data for purposes of identification, and his system, greatly improved and simplified by T. V. Barker, is the basis of the Barker Index (2) which is valuable not only for its determinative tables of crystal angles, refractive indices, densities, and melting points, but also because it contains most of the data for all substances recorded by Groth (corrected where necessary) together with more recent material from other sources, e.g., the tables of Donnay & Mélon (3). Volume 1 (cubic, hexagonal, trigonal, tetragonal, and orthorhombic crystals) has appeared, and volumes 2 (monoclinic) and 3 (triclinic) are in preparation. A card index (4) for the identification of crystalline substances from their x-ray powder patterns has been widely used for some time; it is continually being extended and a program for the substitution of higher-grade reference patterns has now been instituted (5). Identification by x-ray examination of single crystals can sometimes be simpler and more certain than by the use of powder diagrams, and it is perhaps rather surprising that no major attempt has hitherto been made to base a determinative system on it. The single crystal index by Donnay now in press (6) is therefore of great interest and may prove to be the precursor of a comprehensive international index.

The researcher interested in structures is exceptionally well served by the Structure Reports of the International Union of Crystallography (7) and their predecessor, the *Strukturbericht* (8). The latter covers the years 1913–39 in seven volumes. Of the former, which was inaugurated in 1948, volume 11 (1947–48) appeared in 1951, volume 12 (1949) in 1952, and volume

[1] The survey of the literature pertaining to this review was completed in January, 1954.

10 (1945–46) in 1953. Volumes 8 and 9 (1939–44) and later volumes are in preparation. These works describe all structure determinations published in the relevant periods fully enough to make it unnecessary to consult the original papers except where the most minute detail is wanted, and they are comprehensively indexed. An event of considerable importance for all crystallographers is the publication of volume I of the *International Tables for X-ray Crystallography* (9). This work supersedes the *International Tables for the Determination of Crystal Structures* published in 1935; the changes made and the amount of new matter incorporated are so considerable that it must be regarded as a separate publication rather than a new edition. It is an essential tool for all structural crystallographers and a work of great value to many others including students of crystallography. Among many interesting new features of volume I (symmetry groups) is the provision of two alternative descriptions of every monoclinic point group and space group; one of these uses the conventional (and internationally agreed) setting with the *y*-axis as the unique symmetry axis, and in the other the *z*-axis is taken as symmetry-axis (in accord with the convention for the tetragonal and hexagonal systems) for the convenience of workers who may have special reasons for using this orientation. Volume II (Mathematical Tables) is expected to appear in 1954; volume III will contain physical and chemical tables.

In view of the limited availability to many workers of papers in Russian, a review (10) in English of recent Soviet work in the field of crystallography with over 300 references, is welcome, although readers should beware of printing errors.

Methods

There are no major developments in experimental methods to report. The use of counter techniques for intensity measurements continues to increase, and the interest in work at low temperatures has been well sustained. The chief object of the latter at present is the study of simple substances not solid at ordinary temperatures (the average molecular weight of all substances investigated at low temperatures in 1953 was about 60) and this is particularly valuable because it greatly increases the number of cases in which comparison can be made between the dimensions of molecules in the solid state and those obtained by spectroscopy and electron diffraction in the gaseous state. The worth of these comparisons does, however, depend entirely on the accuracy of the analysis, and while the advantage of reducing molecular motion by working at lower temperatures is obvious enough superficially it would be unwise to accept without more searching discussion Burbank's suggestion (11) that a low temperature investigation alone, without special attention to the general problem of reducing the ΔF's, might halve co-ordinate errors. According to Cruickshank's theory (12) the standard deviation of an atomic co-ordinate $\sigma(x)$ is given by

$$\sigma(x) = \sigma(A_h)/A_{hh}$$

where

$$\sigma(A_h) = 2\pi \left\{ \sum_{\mathbf{h}} h^2 (\Delta F)^2 \right\}^{1/2} / aV$$

and

$$A_{hh} = -\partial^2\rho/\partial x^2.$$

The effect of low temperatures is to make the atomic peaks sharper, i.e., to increase the value of A_{hh}, but this will not necessarily reduce the value of $\sigma(x)$ because on theoretical grounds the ΔF's will be expected to increase at low temperatures and they will probably also tend to increase because of experimental difficulties. The comparison between chlorine trifluoride (13) at -120°C. and dibenzyl (12) at room temperature, which Burbank uses to demonstrate the advantage of obtaining high values of A_{hh} at low temperatures, is largely invalidated by the fact that at any temperature the peak curvatures for fluorine and chlorine are respectively about two and five times that for carbon. Since, in principle at least, the ΔF's can be made vanishingly small whereas even at the absolute zero the peak curvature has a finite value, it would seem to be wise, if the aim is high precision in the determination of atomic positions, not to undertake the additional work of experimenting at low temperatures without at the same time making every endeavor to diminish the discrepancy between observed and calculated structure factors. Since this depends on improving the model on which the calculations are based, it is clear that the ideal is to repeat all observations at two temperatures fairly widely separated; in this way the effects of temperature and of inaccuracies in the zero-point atomic scattering factors can be distinguished.

In spite of the demand for quite formidable calculations, arising fron the desire for higher accuracy, the refinement of a structure analysis is now much less laborious and time-consuming than it was a few years ago, because of the increasing availability of electronic digital computers. Applications of general purpose electronic computers to crystallographic Fourier synthesis have been made by Bennett & Kendrew (14) who described methods for the calculation of two- and three-dimensional summations on EDSAC (University of Cambridge), and by Mayer & Trueblood (15) who have used SWAC (Bureau of Standards) for three-dimensional syntheses. Calculations of structure factors have been made by Ordway (16) on SEAC (Bureau of Standards) and by Ahmed & Cruickshank (17) on the Manchester University computer Mark II. A summarized account has been given of the methods used for calculating structure factors on S-FAC (18). These methods have made possible an amount of computation which would previously have been an almost intolerable burden. For example, in 31 min. Ahmed and Cruickshank were able to calculate 1199 structure factors for a triclinic crystal with 19 atoms in the asymmetric unit. The times for Fourier syntheses are in general not quite so impressive because of the relative slowness of putting a

large amount of data into the machine and printing a large number of results out. The method for differential synthesis developed by Ahmed & Cruickshank (17, 19) is considerably faster overall, as it is essentially cyclic when combined with the structure factor program. From a given set of observed F's and approximate atomic positions the co-ordinate shifts (including termination-of-series corrections) are obtained by a sequence of calculations the intermediate steps of which need not be printed or punched out. If the shifts are larger than is regarded as trustworthy or if the structure factors calculated from the new co-ordinates show changes of sign, the whole process can be repeated.

Concurrently with the development of rapid computing methods, a good deal of attention has been paid to thermal motion and its effects (20 to 24) and to errors of various kinds (25, 26, 27). Earlier applications of statistical significance tests to the results of structure analysis were valid for single parameters (e.g., the comparison of a single bond length with a theoretical value) in cases where the Fourier peaks were resolved. Cruickshank & Robertson (28, 29) have now extended the theory to deal with overlapping peaks and to provide many-parameter significance tests. The greater power of multivariate significance tests is well illustrated by the cases of naphthalene and anthracene quoted by Cruickshank and Robertson; the possibility of comparing the molecules as a whole with the theoretical models brings out clearly the fact that there is no significant difference between theory and experimental results for anthracene, but that important errors occur in the theory for naphthalene.

A detailed review of the present state of precision methods of molecular structure determination has been made by Jeffrey & Cruickshank (30) and an outstanding example of the precision attainable in an analysis of moderate complexity has been given by Cochran in his investigation of salicylic acid (31).

Precision analyses can only be made after the approximate structure has been determined and this remains the major difficulty of x-ray analysis—the "phase problem." Much effort has been devoted to attempts to evolve direct methods of structure analysis; Dunitz (32) has given a useful review of work in this field up to the end of 1952, and several interesting papers (33 to 38) appeared in 1953, but a critical assessment of their value cannot yet be made because the relationships between some of the methods proposed have not yet been fully worked out nor have they been tested sufficiently on actual crystal structures. Zachariasen's claim that his method (39) "is not to be regarded merely as still another mathematical formulation of a 'solution in principle' of the phase problem" received support from the analysis of epidote by Belov & Rumanova who report briefly (40) that with its help they were able to determine the signs of 295 out of 350 (h0l) structure factors and so work out the structure without assumptions as to its chemical nature. A full account of this work will be awaited with interest. Methods proposed for determining phases have not so far been cast in a form suitable for

electronic computation, but Cochran & Douglas (41) have now given a preliminary account of a method developed for use with EDSAC which has been tested successfully on salicylic acid, and accounts of other high speed machine methods may confidently be expected to follow. Since most algebraic and analytical methods of sign determination consist in testing a very large number of possibilities and rejecting most of them there should be very little printing-out to do with a properly designed program and it should be possible to take full advantage of the very high speed of actual electronic computing.

In spite of the considerable effort devoted to the theory of direct sign determination the ungrateful majority of crystallographers continue to use the heavy atom technique, Patterson syntheses, and trial-and-error methods with considerable success. Fourier transforms are being increasingly used for trial-and-error analysis particularly by H. Lipson and co-workers who have developed and used optical methods very extensively (42, 43, 44). Hitherto optical methods have been essentially two-dimensional but Kenyon & Taylor (45) have shown how a model of a three-dimensional weighted reciprocal lattice of naphthalene may be used to determine the orientation of the molecules. While this is an important advance it should not be overlooked that, in this case, and those of a good many other aromatic substances (which constitute the majority of crystals so far dealt with by means of Fourier transforms), the molecular orientation can be determined with reasonable precision simply by measuring the magnetic anisotropy, or even the birefringence.

Inorganic Compounds

Details of the re-examination of β-selenium have now been published (46) confirming that it contains puckered Se_8 rings as in the α-form, and not chains as previously suggested. Tucker & Senio (47) have made a more detailed study of β-uranium which leads them to conclude that its structure is not the same as that of the σ-phase alloys, and to reaffirm previous views (48) that the crystal structure is the same in the pure metal as in the β-phase low chromium alloys. Ellinger & Zachariasen (49) have determined the crystal structure of samarium and find that it has a three-atom rhombohedral unit cell but is very nearly close-packed with a mean atomic radius of 1.804 Å. According to a preliminary report (50), white phosphorus at $-30°$ C. has a cubic unit cell containing 224 P atoms.

A critical re-examination of the data for LiH has led Bijvoet & Lonsdale (51) to the conclusion that, contrary to earlier suggestions, the state of ionization of Li and H in this compound cannot be determined by x-ray analysis; the *f*-curves for the neutral atoms and ions differ appreciably only at low angles where no reflections occur. The fluorides of a number of rare earths have orthorhombic structures resembling that of cementite Fe_3C but with different co-ordination numbers (52).

There are conflicting reports about the structure of sodium superoxide

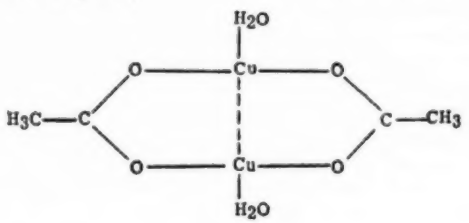
NaO_2. It is polymorphous, and Carter & Templeton (53) have characterized three forms having the marcasite, pyrite, and disordered pyrite structures, respectively, in order of increasing temperature. Zhdanov & Zvonkova (54) obtain somewhat different cell dimensions for the two higher forms and conclude that the highest form has a rocksalt type structure, i.e., that the O_2 ions (with O—O = 1.31 ±0.03 Å) are rotating with spherical symmetry as opposed to the restricted motion required for the pyrite structure. Hoch & Johnston (55a) have succeeded in obtaining x-ray photographs of silicon monoxide SiO which show that it has a cubic lattice with $a = 7.09$ Å at 25°C. The oxide was prepared and photographed at 1300°C. ($a = 7.135$ Å); it disproportionates to Si and SiO_2 very rapidly on cooling, but by quenching from 1300° to 850°C. in two seconds Hoch and Johnston were able to get the room temperature photograph.

More information about several heavy metal oxides has been obtained. α-PbO_2, obtained by electrolytic deposition on platinum, nickel or iron anodes, is found by Zaslavskii & Tolkachev (56) to have an orthorhombic structure related to that of columbite $FeNb_2O_6$. UO_3, which is usually amorphous, is reported by Pério (57) to crystallize on prolonged vacuum heating into two forms, orthorhombic and tetragonal, and by heating a mixture of platinic acid and sodium nitrate for three months at 350°C. Busch and coworkers (58) have obtained crystalline PtO_2 which, on the basis of powder photographs, is said to be hexagonal with a disordered arrangement of linear –Pt–O–O–Pt–O–O–Pt– chains. In OsO_4 four oxygen atoms are probably situated tetrahedrally around each osmium (59). A new and simple structure type for metallic oxides of composition A_6BO_8 has been reported by Kasper & Christ (60). The cubic unit cell contains 32 oxygen ions in an essentially close-packed arrangement and the 28 metal ions are distributed in an ordered way over 28 of the 32 octahedral interstices. The representatives known so far are Mg_6MnO_8 and Cu_6PbO_8 but others should be possible. A more detailed account of the analysis of N_2O_2 reported last year has now been published (61); a study of N_2O_3 (62) could not be carried very far as the structure proved to be disordered. The rare earth oxychlorides have the tetragonal PbFCl type of structure (63) but mercuric oxychloride $2HgCl_2 \cdot HgO$ is reported to have a cubic structure with an atomic arrangement corresponding to $[(ClHg)_3O]Cl$ (64). Abrahams & Grison find (65) that cesium hexasulphide Cs_2S_6 has an interesting ionic structure containing linear S_6^{--} ions of roughly helical shape with bonds which alternate in length (2.02 and 2.11 Å). They assume the 2.11 Å bonds to be pure single bonds and with various other assumptions they calculate the bond order for the short bonds and establish a bond order/length curve for sulfur. On the available evidence, however, this curve can only be regarded as provisional.

The interatomic distances in nitric acid monohydrate (66), although interpreted by Luzzati in terms of nitric acid and water molecules, are, within the rather large probable error of the measurements, consistent with the structure $(NO_3)^-(H_3O)^+$ required by the results of nuclear magnetic resonance experiments by Richards & Smith (67a) and the infrared results

of Bethell & Sheppard (67b). Luzzati has now carried out a more accurate structure analysis of the trihydrate (68) and has been able, by locating the hydrogen atoms, to show that one of the "water molecules" has three hydrogen atoms at bonding distances and is therefore presumably an $(OH_3)^+$ ion; the NO_3 groups deviate very little from the trigonal symmetry to be expected for a nitrate ion. As perusal of any critical discussion such as that by Wells (69) shows, our knowledge and understanding of the bond-lengths in the oxy-acid ions is not nearly as good as it should be, and additions to our knowledge come very slowly. How unexpectedly difficult it may be to obtain results of high accuracy is shown by the investigations of Carpenter (70) and Truter (71) on sodium nitrite; this is a structure of only three parameters, but the intensities are relatively insensitive to the position of the nitrogen atom which could not therefore be located with the precision to be expected in so simple a structure. It appears certain, however, that the N—O bond length lies in the range 1.21–1.26 Å so that it is very closely the same as in the nitrate ion but definitely longer than in the nitronium $(NO_2)^+$ ion (72), as would be expected. An early determination of the structure of potassium and sodium chlorates by Zachariasen (73) showed that the ClO_3 ion was a low pyramid with Cl—O distances of about 1.5 Å; Kartha (74) has now made a detailed study of barium chlorate and bromate monohydrates from which he concludes that the Cl—O distance is 1.57 Å and that the Cl atom lies 0.45 Å from the oxygen plane.

Iron enneacarbonyl, $Fe_2(CO)_9$, was shown by Powell & Ewens (75) to have a bridged structure in which each of the two iron atoms lies at the center of a (somewhat distorted) octahedron of six carbon atoms, three of them being common to each octahedron. This appears to make each iron atom ferric, with six bonds, but it was pointed out by Ewens (76) that the magnetic properties and the short (2.5 Å) Fe···Fe distance make the assumption of a seventh bond between the two iron atoms almost inevitable and he predicted that cobalt tetracarbonyl $Co_2(CO)_8$ should have the same type of structure but with only two bridging CO groups. This has now been verified by Cavalca & Bassi (77) who find that the Co···Co distance is 2.53 ± 0.04 Å. A very interesting bridged arrangement has been found by Van Niekerk & Schoening (78) in hydrated cupric acetate $Cu_2[CH_3(COO)]_4 \cdot 2H_2O$. The two copper atoms are joined by the four acetate groups so that opposite pairs lie in a plane,



I

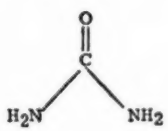
the two planes intersecting at right angles in the Cu—Cu axis which also contains the H_2O molecules, as shown (I). The Cu—Cu distance of 2.64 Å indicates that some direct Cu—Cu bonding is likely so that each copper atom is bonded octahedrally to another copper atom, four oxygen atoms of four different acetate groups, and one water molecule. Quite independently, Bleaney & Bowers (79) concluded from the magnetic properties of cupric acetate that it contained isolated pairs of copper atoms coupled by exchange forces and each surrounded by four oxygen atoms in a plane; the direction of the Cu—Cu axis which they deduced differs only by about 1° from Van Niekerk and Schoening's value. Chromous acetate is isostructural with the copper compound (80) but in the nickel, cobaltous (81), and zinc (82) compounds the metal atoms show the usual octahedral co-ordination of six oxygen atoms from acetate groups and water molecules. Godycki & Rundle (83) suggest that the insolubility of nickel dimethylglyoxime may be accounted for by some binding between nickel atoms in adjacent molecules; the distance 3.24 Å is much greater than those discussed above, but possibly not too great for a small contribution from the d^2sp^3 octahedral configuration to be effective. Such a hypothesis would be consistent with the observed pleochroism and with the fact that the copper compound, which is so similar in molecular dimensions, exhibits a different packing arrangement in the crystal and is more soluble.

Organic Compounds

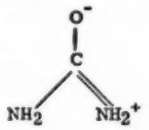
Several complex organic compounds of hitherto unknown or imperfectly known structure have been successfully investigated during the year by x-ray methods. These include nootkatin, $C_{15}H_{20}O_2$, the copper salt of which was studied by Campbell & Robertson (84), β-caryophyllene alcohol, $C_{15}H_{26}O$ studied as the chloride and bromide by Robertson & Todd (85), longifolene, $C_{15}H_{24}$, examined as hydrochloride and hydrobromide by Moffett & Rogers (86) and lanostenol, $C_{31}H_{52}O_2$, which Fridrichsons & Mathieson (87) studied as the iodoacetate. In all these cases previously unknown or doubtful points of structure or stereochemistry were settled unambiguously; it will be noted that the heavy atom technique was used for all, but with such large molecules this is of itself by no means enough to remove all difficulties. In only one case (nootkatin copper salt) was the space group centrosymmetric. The difficulties of investigations of this kind are usually such that atomic positions can be fixed only to about 0.1 Å, which is ample for the solution of stereochemical problems, but Przybylska & Barnes (88) have not only succeeded in clearing up uncertainties in the stereochemistry of α-isosparteine without the assistance of a heavy atom but have determined the bond lengths with a standard deviation of 0.023 Å. The space-group is not centrosymmetrical but the molecule possesses an axis of symmetry, so that the asymmetric unit is about half the size of those mentioned above.

Smith (89) has given a preliminary account of a single crystal investigation of the odd-numbered hydrocarbons from $C_{21}H_{44}$ to $C_{29}H_{60}$. From a de-

tailed analysis of $C_{28}H_{48}$ he finds the distance between alternate carbon atoms in the chain to be 2.549 ±0.004 Å. Vaughan & Donohue have made a careful re-examination of urea (90), as a result of which they find C—O = 1.262 ±0.01 Å and C—N = 1.335 ±0.01 Å corresponding to a molecular structure involving resonance between II and the two forms of III in the proportions indicated. Re-examination of α-oxalic acid by Cox, Dougill & Jeffrey (91) and of oxalic acid dihydrate by Ahmed & Cruickshank (92) show that the central C—C bond in both cases is not significantly different from 1.54 Å (1.56 ±0.01 and 1.53 ±0.02 Å, respectively). Consequently, an explanation of the flatness of the molecule in terms of some double-bond character in the central bond is inadequate. Neither can it be accounted for by crystallization forces (hydrogen bonds) since all three forms, α-, β- and dihydrate, with widely different hydrogen bond systems, have flat molecules. Indeed, as Dougill & Jeffrey have shown (93) the oxalate group is flat in dimethyl



II
40 per cent

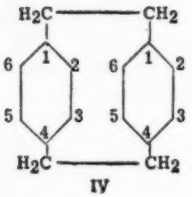


III
30 per cent

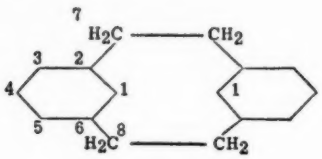
oxalate where ordinary hydrogen bonding is impossible, as it is between oxalate ions which are planar in all structures investigated so far, with the sole exception of ammonium oxalate in which, as Jeffrey & Parry have confirmed (94a), the planes of the carboxyl groups make an angle of about 28°. Some interaction between the polar groups other than conjugation through the central bond seems to be indicated by these results. It is interesting to note in this connection that in α-amino acids the nitrogen atom is almost always found to be in or near the plane of the carboxyl group.

A detailed three-dimensional analysis of maleic acid by Shahat (128) shows that the three C—C bonds are equal within experimental error (1.45 ±0.02 Å); there is an intramolecular hydrogen bond of 2.46 Å between the two carboxyl groups.

Among the structures of aromatic hydrocarbons reported two of the most remarkable are those of di-*p*-xylylene IV and di-*m*-xylylene V described by Brown (95, 96). The para compound was obtained as an unidentified minor product of the pyrolysis of *p*-xylene and its constitution was determined by x-ray analysis. The two benzene rings are not flat; the two pairs of atoms, 1,1 and 4,4 are drawn together by the CH_2—CH_2 links so that they are 0.13 Å out of the 2,3,5,6 planes, which are parallel and 3.09 Å apart. In the meta compound the distortion is of a different kind; atom 1 is displaced about 0.14 Å out of the 2,3,5,6 plane and atoms 7 and 8 are displaced about 0.37 Å on the other side. In this way the nonbonded distance between the



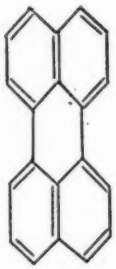
IV



V

1,1 atoms is increased to 2.69 Å. An interesting feature is that atom 4 appears to be displaced slightly (about 0.04 Å) out of the 2,3,5,6 plane on the same side as atom 1, making the ring boat-shaped. In both compounds the bond lengths are normal, averaging about 1.54 Å for the aliphatic bonds and 1.39 Å for the aromatic.

Other aromatic hydrocarbons investigated in detail include ovalene (octabenzonaphthalene) $C_{32}H_{14}$ in which Donaldson & Robertson (97) found a considerable difference between the bond lengths in the center of the molecule (1.43 Å) and those on the periphery (minimum 1.35 Å) which could be accounted for satisfactorily on theoretical grounds. Perylene, $C_{20}H_{12}$ (VI), is particularly interesting because it cannot be formulated with a double bond between the two naphthalene nuclei, so that its central ring might be expected not to display fully the usual benzenoid character; its magnetic properties are in agreement with this expectation. Donaldson, Robertson & White (98) have now carried out an x-ray investigation and although the structure is not favorable to very detailed analysis they find that the two central bonds are distinctly longer (approximately 1.50 Å) than is



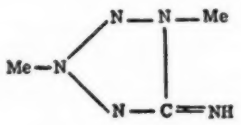
VI

usual in aromatic hydrocarbons. The x-ray results show that the carbon skeleton is flat or very nearly so but the absorption spectrum and the existence of a small dipole moment suggest that the molecule as a whole may not be completely flat. The investigation of diphenylene naphthacene $C_{30}H_{16}$

by Bennett & Hanson (44) is interesting as an example of the successful application of the optical transform methods referred to earlier (42, 43). Stadler (99) has given a good example of the use of molecular transform diagrams in his work on flavanthrone $C_{28}H_{12}O_2N_2$ and Woolfson's investigation of tetraphenylhexapentaene (100) illustrates the use of the concept of the weighted reciprocal lattice (101); the value of measurements of magnetic anisotropy in determining molecular orientation accurately is well shown by the work of Lasheen on naphthalene tetrachloride (102).

Among benzene derivatives the outstanding analysis of the year is undoubtedly that of salicylic acid by Cochran (31), who measured the bond lengths and electron densities with standard deviations of less than 0.01 Å and 0.1 electronic charge per Å^2, respectively, and was therefore able to discuss critically not only the bond structure of the molecule but also its charge distribution. From the point of view of giving guidance to future theoretical developments charge distribution is even more important than bond lengths because the latter cannot be calculated directly except in the very simplest cases.

A number of heterocyclic compounds have been studied. Wiebenga's refinement (103) of the structure of cyanuric acid yields bond lengths in good agreement with those found by Hughes for melamine (104). The analyses of ethylenethiourea (105) and of α-pyridone (106) by Wheatley and Penfold, respectively, approach that of salicylic acid in accuracy and in both cases provide a basis for a critical discussion of the molecular structure. The value of careful assessment of errors is exemplified by Wheatley's discussion of the small deviations from planarity observed in ethylenethiourea. His examination of the relation between hetero-atom bond-lengths and bond orders leads him to the conclusion that at the present time the resonance method provides a more useful basis than the molecular orbital method for the practical purposes of correlating and predicting bond lengths in heteroatomic molecules. The information now available is perhaps scarcely sufficient in quality and quantity to subject this conclusion to a really searching test but in this connection the bond lengths in 1,3-dimethyl-5-iminotetrazole (VII), preliminary results for which have been reported by Bryden and co-workers (107), will be awaited with interest because for "meso-ionic" compounds of this type the molecular orbital representation would appear on general grounds to be preferable to the somewhat artificial valence bond interpretation.



VII

The dimensions of the carboxyl group found by Wright & King (108) in nicotinic acid are not significantly different from those in acetylglycine (109) but are notable for a greater difference (0.15 Å) between the two C—O distances than in any other substance so far reported except formic acid monomer (110, 111). It is also noteworthy that in at least four cases, nicotinic acid, α-oxalic acid (91), oxalic acid dihydrate (92), and acetylglycine, the shorter C—O bond has been reported as less than 1.20 Å which is usually taken to be the length of a 100 per cent C=O double bond, although in no one case is the difference from 1.20 Å significant.

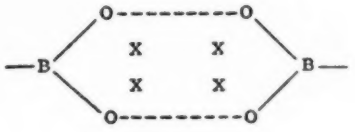
Many papers, too numerous to discuss adequately in this review, have dealt with various aspects of the structures of proteins, polypeptides, and nucleic acids. Among detailed analyses of amino acids may be mentioned α-aminobutyric acid by Hirokawa, Kuribayashi & Nitta (112), N,N′-diglycyl-L-cystine by Yakel & Hughes (113), DL-glutamic acid hydrochloride by Dawson (114), DL-serine by Shoemaker and co-workers (115), an analysis which provides a good example of the value of three-dimensional Patterson syntheses, glycyl-L-tyrosine hydrochloride by Smits & Wiebenga (116), L-glutamine by Cochran & Penfold (117), DL-norleucine by Mathieson (118) and glycyl-L-asparagine by Katz and co-workers (119).

Hydrogen Bonds

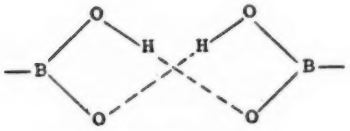
Whereas a few years ago it was considered almost impossible to locate hydrogen atoms in crystals by direct methods, not only has the accuracy of x-ray analysis been improved sufficiently to do it quite regularly, but two new methods have been developed: neutron diffraction and electron scattering from single crystals. In addition, it is possible in favorable circumstances to infer the position of hydrogen atoms indirectly from infrared absorption data or by means of nuclear magnetic resonance absorption. [A comprehensive review of this last subject has been given by Smith (120).] The value of the new methods is enhanced by the fact that they do not merely duplicate the information derived from x-ray analysis but are in large degree complementary to it. It can safely be assumed, in the case of heavier elements, that the centers of the electron clouds which are the atomic positions found by x-rays do not differ from the positions of the nuclei by more than a few thousandths of an Ångstrom unit at most, but this is by no means necessarily the case for hydrogen atoms. Neutron diffraction and nuclear magnetic resonance phenomena give us information about the positions of the nuclei, and electron scattering gives the potential distribution. Thus, the application of these newer methods is likely to be particularly valuable in the study of hydrogen atoms in crystals. [The application of electron diffraction to the solid state has been developed very considerably in Russia by Pinsker and his school (121) but their work has been almost exclusively on polycrystalline material. More recently, Cowley & Rees (122, 123) have developed techniques applicable to single crystal structure analysis.]

One interesting result of recent investigations is that the hydrogen atom

in a hydrogen bond does not necessarily lie on the straight line joining the bonded atoms. This had been thought possible in some cases from the fact that the direction of the O—H or N—H vector determined from polarized infrared absorption did not appear to lie in the direction of the hydrogen bond as determined by x-rays. Cowley's electron diffraction study of boric acid (124) purports to show that the hydrogen atoms in the parallel O—H···O bonds are displaced inwards to the positions x (VIII) (each of which represents $\frac{1}{2}$H because the structure is disordered). Cowley suggests that this is due to contributions such as IX



VIII



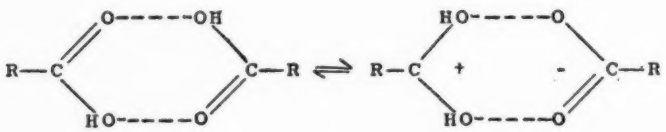
IX

and that similar effects might be found in other systems of parallel hydrogen bonds such as occur in carboxylic acid dimers. This is not borne out by Cochran's work on salicylic acid (31) in which the hydrogen atoms lie within experimental error, on the straight lines joining the oxygen atoms of pairs of carboxyl groups; the O—H bond of the ortho OH group, on the other hand, is displaced nearly 20° outwards from the direct line of the intramolecular O···O bond to the carbonyl oxygen, so as to maintain a C—O—H angle of approximately 109°. (In boric acid the B—O—H angle appears to be rather less than 100°; if the H atoms lay in the O···O directions it would be 120°.) In KH_2PO_4 the neutron diffraction experiments of Bacon & Pease (125) at room temperature, and of Peterson, Levy & Simonsen (126) at 140° K leave no doubt that each hydrogen atom lies exactly in line with the two oxygen atoms bonded by it.

In KH_2PO_4 the hydrogen peak in the Fourier syntheses was found to be circular in section perpendicular to the O—H—O bond and oval in section parallel to it. This might be consistent with a symmetrical bond but could more probably be accounted for by statistical distribution of the H atoms over the two possible unsymmetrical positions. Quite recently, Pease & Bacon (127) have examined a crystal maintained as a single ferroelectric domain by the application of an electric field at 90° K. (below the Curie

point) and find that under these conditions the H atom is situated 0.21 Å from the center of the O—O bonds, i.e., 1.04 Å from one oxygen atom. The displacements from the bond centers are all in the same sense so that the normal tetragonal symmetry of the crystal is reduced to orthorhombic, and when the field is reversed all the hydrogen atoms move to the other side of the bond-center.

Symmetrical hydrogen bonds are possible if the distance is short enough, but in the case of O—H—O bonds the required distance is probably less than 2.5 Å for in maleic acid, where Shahat (128) finds an internal H bond of 2.46 Å, the inequality of the C—O bonds on either side leave little doubt that the bond must be unsymmetrical, as it certainly is in the rather longer (2.59 Å) bond in salicylic acid. Cardwell, Dunitz & Orgel (129) have pointed out however that the removal of a hydrogen ion from maleic acid should encourage the remaining acidic hydrogen atom to move towards the now negatively charged carboxyl group, so that the hydrogen maleate ion should be more likely than the acid to contain a symmetrical O—H—O bond. Their infrared measurements are consistent with this but the more direct evidence of x-ray or neutron diffraction is not yet available. The analysis of nickel dimethylglyoxime by Godycki & Rundle (83) did not show the positions of hydrogen atoms but the shortness of the internal O—H—O bond (2.44 Å) combined with the spectroscopic evidence of Rundle & Parasol (130) suggests that this bond may be symmetrical. The crystallographically symmetrical intermolecular hydrogen bonds found in various acid salts by Speakman and co-workers (131) are almost certainly only statistically symmetrical. Harris & Alder (132) have discussed the temperature variation of the dielectric constant of liquid carboxylic acids and conclude that a proportion of dimers are self ionized as shown (X); it is to be hoped that in interpreting their results for solid acids crystallographers will not have to take account of this possibility in a situation which is already complicated enough.



X

Lord & Merrifield (133) have reviewed the evidence from infrared absorption and show that there is a linear relation between O—H—O or N—H—O bond length and the O—H or N—H frequency shift (taking 3700 cm.$^{-1}$ and 3400 cm.$^{-1}$, respectively, as the standard O—H and N—H frequencies unaffected by H bonding). They conclude that these and other results (e.g., the evidence for strong N—H····Cl bonds in tertiary amine hydrochlorides) are incompatible with a simple electrostatic model for the

hydrogen bond and that a quantum mechanical model is required. A one-dimensional wave equation for H bonds has, in fact, been treated briefly by Nordman & Lipscomb (134) who have pointed out the importance of developing a quantum treatment for, inter alia, the isotope effect which they and also Rundle (135) have discussed in relation to the thermal expansion of crystals.

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SURFACE CHEMISTRY AND CATALYSIS[1]

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The period covered by this review extends from December 1, 1952 through November 30, 1953. The general level of activity in surface chemistry and catalysis is approximately the same as in the immediate past. Two changes have been observed in the field of surface chemistry. Investigations of the thermodynamic properties of the surfaces of solids, both experimental and theoretical, are on the increase. A large fraction of the investigations were not completed in time for publication in the period covered by this review. The results should appear in the journals in 1954. Studies of physical adsorption have not been so greatly restricted to the determination of equilibrium isotherms as in the past. A larger fraction of the studies were devoted to kinetics and other problems. The additional techniques which are now being utilized show promise of yielding valuable information which could not be obtained from simple adsorption studies.

Jura & Garland (1) presented a method by which the free surface energy, surface entropy, and enthalpy of a finely divided solid could be experimentally determined. The measurements which are necessary are an area determination, the heats of solution and heat capacity determinations of the finely divided solid and of a sample of the same solid which is sufficiently coarse that it can be considered to have zero area. If the area of the finely divided solid is A, and ΔC_p and ΔH_{298} are the differences in specific heats and heats of solution of the two samples of solids, the enthalpy, h, surface entropy, s, and free surface energy, γ, are

$$h_{298} = \Delta H_{298}/A$$

$$h = h_{298} + \int_{298}^{T} \Delta C_p \, dT$$

$$s = 1/A \int_{0}^{T} \Delta C_p/T \, dT$$

$$\gamma = h - Ts$$

The determination of the enthalpy at room temperature is an old measurement. The best known such measurements are those of Johnson, Lipsett & Maas. Giauque showed that the entropy at 0°K. was independent of particle size.

The necessary measurements were made for magnesium oxide. The sample used was contaminated both in the bulk and on the surface by magnesium hydroxide. It was found that the enthalpy increased from 1040 ergs cm.$^{-2}$ at 0°K. to 1090 ergs cm.$^{-2}$ at 298°C., the free surface energy decreased

[1] The survey of the literature pertaining to this review was completed in November, 1953.

from 1040 to 1000 ergs cm.$^{-2}$ in the same temperature interval, and the surface entropy at the higher temperature was 0.28 ergs cm^{-2} deg $^{-1}$.

Bauer (2) criticized the use of the above theory in that no account was taken of possible crystal imperfections. He argued that the number of imperfections could be a function of the size of the particles, and that the values obtained by this method might not be valid. Jura & Garland (3) expressed the belief that the effect of crystal imperfections would be smaller than the precision now available in making the necessary measurements. Bauer actually pointed out a serious problem. The problem is: can we speak of the thermodynamic properties of the surfaces of solids in the same manner in which the terms are applied to the liquid state? Are the values for the surface properties of a solid unique regardless of the size of the particle or method of manufacture? The last holds only if the same crystalline face is considered. Experimentation on this is now in progress.

There have been no major new developments in the determination of the surface tension of solids from stress measurements nor of the relative interfacial energy from the orientation of several grains.

No reports were made which further explore the configuration of the molecules in the surface of a solid. Two quantum mechanical treatments of the surface energy of metals were published. Ewald & Juretschke (4) made no numerical computations. Stratton (5) used a more elaborate model and obtained numerical answers for the surface tension of metals. His values were all considerably lower than the best available experimental data. The experimental data may not be too good. The models used in the above treatments are too simple. Perhaps in time it will become possible to utilize more realistic models.

In passing, it is of interest to note that Reference 4 contains many extensive reviews and original papers on the surface of solids through late 1952.

Jura & Pitzer (6) made a theoretical investigation of the heat capacity near 0°K. The limitation of this treatment is the validity of the Debye model. They pointed out that for a finely divided solid at these temperatures an additional term would have to be considered in the computation of the heat capacity arising from the motion of the crystallites. Each particle must have three degrees of rotational and translational freedom. Because of the confinement of the particles in a calorimeter, the translation would of necessity be a vibration, and the rotation an oscillation. This would mean that there would be a contribution to the heat capacity of $6k$ for each particle at any temperature sufficiently high that these motions could be considered as classical. The estimates of this temperature for the relatively large masses involved in a crystallite lead to the conclusion that the motion is classical at any readily obtainable temperature. For cubical aluminum particles, 100 Å on edge, they found that the contribution to the heat capacity was about 50 times that of the normal crystal vibrations at 1°K. At higher temperatures, this quantity becomes negligible. One result of this investigation is that at the lowest temperatures, the surface entropy of a finely divided solid is a

function of the degree of subdivision as well as temperature. This dependence on the degree of subdivision is very small, and at reasonably high temperatures becomes negligible.

In the same paper it was shown that at the lowest temperatures it was necessary to quantize the standing waves. A continuous frequency distribution utilized by Montroll becomes valid at several degrees Kelvin but cannot be used near the limit of 0°K.

A Debye treatment of the heat capacity as a function of size was proposed by Stratton (7). In his paper a complete Debye frequency distribution function is developed. Since the Debye theory cannot reproduce the observed specific heat with precision, the surface heat capacities could easily be in error by several hundred per cent or more. If an order of magnitude of the surface entropy is desired, then this would be a satisfactory technique. But it is not reasonable to expect to obtain values of any precision.

Two experimental problems in physical adsorption have been given a fair amount of attention. The first is the existence of discontinuities in the adsorption isotherm at low pressures and coverages first reported by Jura *et al.* (8). In this period Corrin (9) investigated the adsorption isotherms of *n*-heptane on ferric oxide from 16.55° to 29.55°C. He did not observe any discontinuities where they had been previously reported. Young, Beebe & Bienes (10) studied the adsorption of *n*-heptane on graphite and ferric oxide. These authors also could not find any discontinuities. All of the above workers conclude that such discontinuities do not exist. Another investigation by Utsugi (11) of the adsorption of ethyl alcohol on various ferric oxide—titanium oxide mixed gels between −5° and 90°C, is apparently the most extensive to date. The gels were heat treated at 150°, 250°, 350° and 450°C. Utsugi found discontinuities similar to those reported by Jura and coworkers, but observed them to be exceedingly sensitive to the composition of the solid. He found that the samples heat treated at 250° and 350° exhibited the discontinuity while the other two samples did not. Since the effect of heat treatment is to change the water content of the gel, he concluded that the exact composition of the solid is the important factor in determining the exact nature of the isotherm at low pressures and coverages. The samples which exhibited the discontinuities showed the same general features as found in the early reports of Jura and co-workers. Even the anomalous temperature coefficient below the discontinuity was reproduced. The critical constants of the two samples that exhibited the discontinuities were determined and found to be different for the two samples.

Utsugi does not state explicitly all of the experimental details, which would be desirable. He used a gravimetric technique with a Pirani gauge for the measurement of the pressure. He also states that there was no variation in the pressure for a period of 12 to 24 hr. after apparent equilibrium was established, and that the isotherms were reversible in the region of interest.

Loeser, Harkins & Twiss (12) studied the adsorption of *n*-propyl alcohol on iron, ferric oxide, and magnetite. The technique was improved over that

used earlier (9), and the discontinuities were found to be present.

The stepwise adsorption found an carbon blocks at high relative pressures, described by Polly, Schaeffer & Smith (13) is a completely different phenomenon from that under discussion in this section.

It is apparent that the question of whether or not such transitions occur in adsorption is still open to debate. If the work of Utsugi is correct, in that small variations in the composition of the solid can change the entire character of the adsorption isotherm in this region, it is evident that the final word on this matter can be had only when several investigators use the same sample.

A relatively large number of publications concerning the adsorption of helium were published in the past year. The behavior of helium is obviously important, since it is in these studies that it becomes possible to evaluate quantum effects and the role of the zero point energy in the adsorption process. The important question which has been apparently settled by this year's work is the exact nature of the isotherms as a function of temperature. Of the seven papers which appeared, the most important is that of Bowers (14), in which he describes the apparatus, techniques, and analysis of the observed data. The method used is essentially a differential gravimetric technique. It is so developed that not even buoyancy corrections are necessary. The amount adsorbed is directly proportional to an observed deflection. The apparatus was used first to study the adsorption of argon, nitrogen, and oxygen near saturation pressures. The results obtained are similar to those obtained by the older techniques. In this study they found that near saturation the isotherms obeyed the Frenkel-Halsey-Hill isotherm,

$$-\ln p/p_0 = K/n^3.$$

The sensitivity of the apparatus used is such that for adsorbents of relatively small areas, the technique cannot be used at low coverages. The apparatus was then used for the determination of the adsorption isotherm of helium both above and below the lambda point (15). The isotherms, from the point corresponding roughly to the adsorption of a single monolayer to saturation, were continuous, and behaved as if one of the higher molecular weight gases were being adsorbed at a higher absolute temperature, even to satisfying the Frenkel-Halsey-Hill isotherm. Also, there was no discontinuity in any function when the temperature passed through the lambda point. In brief, the general appearance of the results was that there was no gross difference between the general behavior of helium and the other gases which have been investigated. Other papers on the same topic have been written by Brewer & Mendelsohn (16, 17, 18), Bowers (19), and Long & Meyer (20).

It appears that the adsorption isotherms of Bowers are generally correct, and that only the precision could be improved. The flow properties of liquid helium films have not as yet been determined without ambiguity. This, and the complete significance of the work, must await the work of the present and future. What appears certain at the present time is that there is a

large change in the zero point energy of helium when it is adsorbed, and that the explanation of the observations must be predicated largely on this basis.

Several calorimetric studies of adsorption were published. There was a continuation of the study of the heat capacity of systems of solids with an adsorbed film. Drain & Morrison (21) investigated films of nitrogen and oxygen on rutile, while Pace, Heric & Dennis (22), and Dennis, Pace & Baughman (23) studied the adsorption of methane on the same solid. The general appearance of the thermodynamic functions obtained from these studies is the same as those from the earlier studies. The results, in principle, for the polyatomic molecules can be carried further. To illustrate, the work of Drain and Morrison can be used as an example. From a consideration of simple models for the estimation of the contribution of the various motions to the entropy, these authors conclude that one degree of rotation of the oxygen molecule is hindered, while both are hindered for nitrogen. The above conclusions depend upon a consideration of the quadrupole solid interaction. This has been evaluated by Drain (24). The important result obtained by Drain, concerning the contribution to the heat of adsorption by the interaction of a permanent quadrupole and an ionic lattice, is that the heat is not greatly affected by the position of the quadrupole over the unit cell in the surface. Drain and Morrison also argue that the data which they have obtained as a function of surface coverage indicate that the surface is heterogeneous. They attempt to get a distribution function of the energy. The most important aspect of the work appears to be the technique of analysis of the data which permitted the contributions of the various molecular motions in the adsorbed state to be evaluated.

Another calorimetric development of interest was the construction of a calorimeter for the measurement of the heat of wetting that utilized a thermistor as the temperature element. The work is that of Zettlemoyer *et al.* (25). The system studied in their paper was the water—asbestos system. The results were normal, in that the general appearance of the curves of thermodynamic properties was similar to those previously published. This calorimeter does not have the precision of that used by Harkins and coworkers, but it appears to have an advantage in that results can be more readily obtained, and it is more versatile so that its use will not be restricted to temperatures close to room temperature. As expected, the authors found that the thermodynamic functions were more precisely determined by the combination of a calorimetric measurement and an isotherm, than from a series of isotherms at different temperatures.

Several experiments were performed that shed some light on the nature and the structure of the surfaces of solids. These investigations with fuller development, show promise of becoming valuable adjuncts to adsorption and other measurements in the determination of the nature of the surfaces of solids, and possibly heterogeneous catalysis.

Pimentel, Jura & Garland (26) investigated the infrared adsorption

spectra of heavy water adsorbed on the surface of silica gel. The technique used by these investigators was such that they could observe only the region around 2600 cm.$^{-1}$. The ν_3 band of D_2O is in this region. They made observations when the surface coverage varied from 0.05 to 1.8 monolayers of adsorbed D_2O. Below 0.3 monolayers of adsorbate there was general adsorption, but no structure. Above 0.3 monolayers, the absorption band was, within experimental error, the same as in liquid D_2O. The absorption at low coverages is direct experimental evidence of the heterogeneity of the surface. With respect to the perturbation of the single band under observation, it is possible to state that approximately 20 per cent of the surface is sufficiently energetic to perturb the internal motion of the adsorbed molecule to varying degrees. Perhaps the most important result of this investigation was the fact that the exchange of the adsorbed D_2O with the H_2O in the gel could be observed and followed with time. If the technique could be extended so that these observations could be made on more complicated systems and at all possible frequencies, it is probable that information of value concerned with catalysis could be obtained by this method.

Two related papers on the determination of the surface potential of semiconductors yielded results which may prove to be of prime importance in the study of the surfaces of solids and the role of many solid catalysts. Brattain & Bardeen (27) measured the variation in contact potential of germanium as the ambient gas was varied, while Morrison (28) measured the change in conductivity of the same systems. Since the two papers cover the same subject, and Bardeen was aware of, and participated in the discussions of, the paper by Morrison, the results of the two are combined into a single discussion.

Experimentally, it was found that the contact potential between the germanium sample and a reference platinum electrode depended upon the ambient atmosphere. In the interpretation of the results, the authors assumed the gases to be chemisorbed on the solids. Although they did not attempt to measure the amount of gas adsorbed, nor even to verify that adsorption had occurred, it is entirely plausible from the temperature and the nature of the molecules that some adsorption had taken place. The contact potential was the most positive for molecules containing the –OH group, and the least positive for ozone and peroxides. On illumination the change in the contact potential was the greatest for N-type germanium when the surface was the most negative, while the opposite was true for P-type germanium. The resistance of the samples followed essentially the same pattern. The variation of the resistance was greater and more time-dependent than the contact potential.

To explain the above results, it has been assumed that there is a space charge layer in the solid which gives rise to a potential V_B and an additional potential due to the dipole formed by the sample and the adsorbed molecules, V_D (27). The contact potential, c.p., is then given by the equation c.p. = $V_B + V_D + \text{const}$. Because of the variation in the number of defects from

sample to sample, the absolute magnitude of the contact potential is not critical in the interpretation of the results, but rather the variation of this quantity with respect to a third variable, namely, the intensity of light. This means that the results will be qualitative in nature. However, our knowledge of the structure of the surfaces of solids is such that even qualitative information is of great value.

The work shows that there is a change in shape of the valence and conduction bands at the surface of the solid, and that the adsorption also leads to a change in the shape of the bands. The importance of this conclusion for the understanding of the nature of the surfaces of solids is paramount. Of equal possible importance is the extension of this work to heterogeneous catalysis. Many catalysts are semiconductors. It is evident from this work, that the adsorption process changes the levels of the bands at the surface. Consequently, the number of electrons that become available for chemical reactions are affected by this change. Thus, it can be readily argued that when a semiconductor is the catalyst, it is likely that the solid itself partakes in the reaction. This has been strongly argued in recent years. If band structure can be determined in future work, it may become possible to extend these results directly to the prediction and understanding of many catalytic reactions. It is to be hoped that these and other investigators fully explore these measurements.

Several papers on kinetics appeared in the past year. Both experimental and theoretical papers have been published. Perhaps the most significant paper on kinetics which has appeared in the last decade is that of Sutherland & Winfield (29). They consider in detail the kinetics of gas flow through a porous medium when (*a*) adsorption is too fast to be the rate determining step; (*b*) there is chemisorption and the rate is controlled by the gas flow; (*c*) there is unrestricted chemisorption. In all of the above it is assumed that the gas flow is Knudsen flow. Since this is usually the condition that exists in catalytic reactions, the treatment can be considered to be quite general. It is not possible in this relatively short space to outline completely the treatment of these authors. The problem that they treat and solve is as follows. Consider a large granule that is permeated with pores. There is an ambient pressure of P_0 around the particle. The gas diffuses into the pore, is adsorbed, reacts, is desorbed, and the product diffuses out of the pore. There is a consideration of the local pressure, p, at the adsorption site. The treatment is such that the actual chemical rate can be obtained from the necessary observations. For example, it would be applicable to the treatment of the rate of reaction of oxygen with a rod of graphite. In spite of the generality of this treatment and the number of variables that have been considered, it is possible to evaluate all of the necessary quantities.

Of equal importance to the experimentalist is the development of a technique for the rate of adsorption of gases when the rate of adsorption is quite rapid. The work is by Winfield (30). In brief, the method utilizes a diaphragm capacitor as the pressure measuring device. The graphs shown in the paper

indicate that times on the order of 0.001 sec. can be determined with precision. In order to obviate the difficulty of having the gas measured out in one part of the system and then transported to the adsorbate, the gas is held in an ampoule in the same chamber that holds the adsorbent. Using this method, it is possible to make precise measurements even at low pressures. Since an oscilloscope is used to measure the variation in the capacitance of the pressure gauge, it is apparent that the only time limitation on this technique is the response time of the glass or quartz diaphragm which may be used by the experimentalist. Also, since a metallic coating is necessary, gases which would react with the metal cannot be used. This, however, is a minor limitation.

In the third paper of this series, Sutherland & Winfield (31) utilized the results of both previous papers. They studied the rate of adsorption of water at 140° C. on alumina and thoria. For shallow beds, the results between observed and calculated results are exceedingly good. For a deep bed, the results are not as satisfactory. However, a perusal of the single curve shown indicates that in complete absence of any information, the rate could be obtained within an order of magnitude.

The problem treated by Sutherland and Winfield involves the flow of gas in a capillary. Barrer (32) has also treated this general problem. In his paper emphasis is placed on the measurement of the time lag. This is the time which would be obtained if the steady-state flow curve were extrapolated to zero transport. The major difficulty with this method is the ignorance of the actual structure. If the so-called tortuosity factor is estimated as usual at roughly $2^{1/2}$, then reasonable results can be obtained from the flow data for internal areas of the solid. Consistent data can be obtained. In the above paper the equations are solved for the separation of gases of different molecular weights by the use of a bed of porous materials. Several such separations were reported. In a later paper, Barrer & Robins (33) studied the separation of gases by the use of $Na_2O \cdot Al_2O_3 \cdot 10SiO_2 \cdot 6.6H_2O$ as a molecular sieve.

Other papers involving kinetics with some theoretical interest are by Patterson (34) who has discussed surface diffusion; and Ely (35) who has considered chemical adsorption. In this latter paper the adsorption is a particular phase of a more general treatment of reactions in a condensed phase. The rate of adsorption of krypton on glass spheres at low pressures was determined by Liang (36). He found that it took approximately two days to attain equilibrium. He did not attempt an analysis of the data.

Another kinetic study of some importance is the series of papers by Addison & Litherland (37), who used surface tension and contact potentials of solutions as a method of investigation of the kinetics of spreading. They found that the potential changed even after the surface tension became apparently constant. They suggest that the surface tension is relatively insensitive to some possible changes. The changes in potential are due to the change in the orientation of the molecules at the surface. The surface tension apparently becomes fixed when the number of molocules per square centimeter is constant, irrespective of the orientation of the molecules.

The possible application of the field emission microscope to surface study and catalysis has been considered. Becker & Hartman (38) discussed the general possibilities of the tool. Their paper is a general exposition of its use rather than a detailed investigation of any single system. Rates of adsorption and sticking probability are the most important topics developed. Gomer (39) has used this technique to study the chemisorption of oxygen on tungsten. He showed that chemisorbed O_2 became mobile only above 350°C. while physically adsorbed O_2 was mobile at the temperature investigated. It is apparent that this instrument will have its uses, and will furnish some information of value. It appears, however, that relatively few questions will be answered in an unambiguous manner by this technique alone. The methods required for its proper operation are such that for several years the data available will come primarily from those few now engaged in such research.

Three papers were published reporting the study of mixed adsorption. Ryerson & Honig (40) studied the adsorption of NO_2-N_2O_4 on rutile. This is one of the simplest of all systems, since the equilibrium constant is well known. One important finding of this investigation is that rutile loses oxygen when heated in vacuo. It has been long known that rutile is usually oxygen deficient, but the fact that it can continue to lose oxygen upon prolonged heating indicates that there are certain experiments which may seriously be affected by this varying departure from stoichiometry. Since many recent researches have used this solid, it is possible that discrepancies may be found in the event that another investigator attempts to repeat an experiment.

Barrer & Robins (41) studied the mixed adsorption of several pairs of gases on chabazite and mordenite. The pairs of gases investigated were taken from H_2, Ne, N_2, O_2, and A. The behavior could not be correlated with the predictions made from the Langmuir isotherm. More elegant treatments were not attempted. Glueckhauf (42) reported a theoretical treatment of mixed adsorption. The model that he uses is an extension of the Halsey treatment for the adsorption of a single adsorbent on a heterogeneous surface. He uses the Freundlich isotherm and a distribution function of the energy of the various adsorbing sites. It is to be hoped that these results will be applied to some of the earlier experimental data to see if these ideas are as successful in this application as in the one gas system.

There have been many excellent papers on the determinations of adsorption isotherms and calorimetric work, but they have tended to confirm the present pictures of adsorption rather than to add any new or startling ideas. They have enriched the over-all picture by adding needed detail.

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THE MICROWAVE SPECTRA OF GASES[1]

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It was necessary for spectroscopists to wait for the techniques developed during World War II before they could explore extensively the microwave region. Since the war much of this region has been ranged and a great deal of new and accurate information on both molecules and nuclei obtained. Bond distances, nuclear quadrupole coupling constants, moments of inertia, nuclear spins, dipole moments, and internal rotation barriers form only a partial list of the physical properties that have been evaluated through microwave spectroscopy. During the year 1953 this field of research has continued to grow. New physical properties have been measured and new molecules explored. In this report we shall attempt to evaluate the progress made over the last year and to summarize the scope of the field.

Experimental

Without doubt, the most important single advance in the experimental aspects of microwave spectroscopy was made about six years ago with the development of Stark modulation. This technique increased instrument sensitivity by over a thousandfold and it made possible most of the work reported in the present and past reviews. The developments made in millimeter wave spectroscopy this year, while not as startling an advance in instrumentation as that of Stark modulation, may ultimately have as great an effect upon future research.

The majority of measurements made by microwave spectroscopists have been in the region of 1.6 to 0.6 cm. of wave length. A series of klystron oscillators produces sufficient power over this region, but for shorter wave lengths such sources are not available. To go further into the millimeter region the output from these oscillators has been passed through suitable rectifying crystals and the resultant harmonics filtered by short sections of wave guide. The difficulties associated with this technique center around the construction of the rectifying crystal and the natural consequence of smaller available power associated with each higher harmonic.

During this past year the groups at Columbia and Duke Universities have made advances in the technique of harmonic generation. King & Gordy (1) have measured new rotational lines for OCS, CH_3F and H_2O in the 1–2 mm. region. They report that their harmonic generators are broad banded, thus eliminating a great deal of adjustment with a frequency change. Klein & Nethercot (2) have measured the three iodine nuclear quadrupole multi-

[1] The survey of the literature pertaining to this review was completed on January 15, 1954.

[2] The authors would like to thank Mr. Jose Fernandez for assistance on the preparation of the tables and the bibliography.

plets of the lowest rotational transition for DI. Burrus & Gordy (3) report measurements on H_2S^{32}, H_2S^{33}, and H_2S^{34} in the 1–2 mm. region on samples with normal isotopic abundance. The quadrupole coupling constants reported for H_2S^{33} are particularly interesting and will be commented on later. In unpublished reports, further work in the millimeter region has been done on DBr, DI, NO, and PD_3 (4).

The problem of obtaining the microwave spectra of molecules at temperatures near 800°C. has been an interesting development over the past few years. The experimental difficulties have been many, but as a means of obtaining accurate data on the alkali halides this research has been invaluable. The latest report by the group at Columbia University is by Honig, Stitch & Mandel (5). They report data on CsF, CsCl, and CsBr.

High resolution has always been one of the advantages of microwave spectroscopy. The work this year has set a new high in high resolution with the measurement of the nuclear quadrupole interaction of the deuteron. White (6) has reported accurate quadrupole coupling constants for deuterium in DCCCl and DCN. Such nuclear interaction was probably observed also by Beers & Weisbaum (7) in HDO. Kisliuk & Geschwind (8) report high resolution work on AsF_3 in which both first- and second-order nuclear quadrupole and nuclear magnetic dipole interaction was resolved and measured.

Theoretical

One of the most interesting theoretical problems in microwave spectroscopy is that of centrifugal distortion. A great deal of the high precision of microwave work is lost because of the large centrifugal distortion corrections that often have to be applied to the experimental frequencies. These distortion corrections are particularly large for molecules with small moments of inertia, e.g., H_2O and PH_3. Kivelson & Wilson (9) have published a method of obtaining the centrifugal distortion constants from the valence force potential function. This supplements their previous paper (10) dealing with the Hamiltonian for centrifugal distortion. In another paper submitted for publication, Kivelson (11) has applied these techniques to SO_2. He has been able to obtain excellent agreement between the experimental and calculated frequencies, and he has even obtained some good estimates of the vibrational frequencies of SO_2 from the microwave data. For the symmetric top molecule, CH_3Cl, Chang & Dennison (12) have improved the previous calculation, from infrared data, of the centrifugal distortion constants D_{JJ} and D_{JK}. In this new calculation based upon a revised normal coordinate analysis they obtain excellent agreement between the observed and calculated D_{JK} values. However, they obtain only fair agreement for D_{JJ}. Since the value of D_{JJ} is dependent in a very simple manner upon the infrared frequencies, they believe that the microwave value for D_{JJ} is in error. Centrifugal distortion corrections have also been applied to PH_2D and PD_2H (13), HDO (7, 14), and HNCS (15).

The combination of hyperfine structure and Stark effect is often encountered in microwave spectroscopy, and Mizushima (16) has published a treatment of this problem that is applicable to asymmetric tops. In two papers by Mizushima & Venkateswarlu (17) they consider possible microwave absorption by molecules with D_{2d} and T_d symmetry. They show that absorption is possible in certain cases, but that the absorption coefficient is relatively small. No such absorption has yet been detected. The small Zeeman effect of H_2O, HDO, and D_2O has also been shown to be in theoretical agreement by Burke & Strandberg (18).

Hicks, Turner & Widule (19) have applied a large digital computer to the problem of asymmetric rotor energy levels. They have tested procedural methods and have circulated among spectroscopists an energy level table for κ intervals of 0.01. This table is 10 times as large as that of King, Hainer & Cross (20), and it should be of considerable computational assistance. Additional theoretical papers have dealt with hindered rotation by Burkhard (21), absorption line broadening by Danos & Geschwind (22) approximate asymmetric top energy level formulae by Kivelson (23) and nuclear quadrupole interaction for two spin 3/2 nuclei by Robinson & Cornwell (24).

Spectroscopic Results

Gordy, Smith & Trambarulo (25) have written the first book on the subject of microwave spectroscopy. It is the most extensive review that has been written to date and it should prove to be a valuable reference. The tables of spectral results that appear in the appendix are very complete.

Linear molecules.—In Table I a list of linear molecules is given together with the results of microwave investigations made over the last year. Most

TABLE I

Linear Molecules

Formula*	Experimental Results†	References
$O_2^{16,18}$	$B_0=43{,}102\pm5$ Mc. from spin interaction	(26)
$O_2^{16,17}$	measured O^{17} magnetic fine structure	(26)
DI	$B_0=97{,}535\pm5$ Mc.	(2)
CsF	$r_e=2.3483\pm.0001$ Å	(5)
CsCl	$r_e=2.9062\pm.0001$ Å	(5)
CsBr	$r_e=3.0720\pm.0001$ Å	(5)
OH	measured Λ doubling	(28)
OCS	$D_J=1.294\pm.005$ kc.	(1)
DCN	measured deuterium quadrupole interaction	(6)
DCCCl	measured deuterium quadrupole interaction	(6)

* Unless specified, data are given for molecular species containing the most abundant naturally occurring isotopes.

† For quadrupole data see Table IV

molecules absorb microwaves through the interaction with molecular electric dipole moments. However, in the case of oxygen the interaction is through the magnetic dipole moments of unpaired electrons. Because of the unpaired electrons a pure rotational spectrum is not observed for oxygen, and the spectrum that is obtained is a combination of electronic and rotational energies. Miller & Townes (26) have refined the theory of the energy levels of oxygen and they have obtained a better agreement between the observed and calculated microwave absorption spectrum for $O^{16}O^{16}$. A magnetic fine structure was found in the case of $O^{16}O^{17}$. This is the result of the further interaction of the nuclear magnetic moment of O^{17}. Miller, Townes & Kotani (27) have based speculations as to the electronic structure of oxygen upon this magnetic fine structure. This paper will be discussed later.

The free radical, OH, has been observed to have absorption in the 1.25 cm. range by Sanders *et al.* (28). These OH radicals were generated by a radio frequency discharge through water, and the absorption was measured in a special glass wave guide cell. Since this is the first microwave work that has been done on free radicals it is an historic event, and it may open the way for further free radical absorption spectra.

Symmetric top molecules.—One of the valuable results obtained from microwave spectra is molecular dipole moments. These dipole moments are determined for a specific isotopic species of a molecule and within a given vibrational state. In addition, the values of the dipole moments are almost completely independent of assumptions concerning electronic and atomic polarization. Ghosh, Trambarulo & Gordy (29) have determined the dipole moments of eight symmetric top molecules from the Stark effect of their microwave spectra. In addition, the dipole moments of many other linear, symmetric, and asymmetric top molecules have been determined from microwave spectra, and these values are often compiled in the usual summaries of electric dipole moments.

In order to determine the structure of a molecule from its microwave spectrum it is usually necessary to combine data from more than one isotopic species. For example, consider a substituted methane of the type Z_3CX. This molecule is a symmetric top and from its microwave spectrum one can determine only the moment of inertia which is perpendicular to its symmetry axis. This moment of inertia is dependent upon three structural parameters X–C distance, C–Z distance and ZCZ angle. However, it is not possible to determine these three parameters from a single moment of inertia. Therefore, one usually determines the moments of inertia of three or more isotopic species and combines the data to give three consistent structural parameters. This procedure is illustrated in Table II by the work of Bak, Bruhn & Rastrup-Andersen (33) on H_3SiF. The moments of inertia of $H_3Si^{28}F$, $H_3Si^{29}F$, $H_3Si^{30}F$, $D_3Si^{28}F$, $D_3Si^{29}F$, and $D_3Si^{30}F$ have been determined from their microwave spectra. Because of zero-point vibration the effective bond distances do change with an isotopic substitution. The six moments of inertia for the six isotopic species of H_3SiF are not consistent with only three structural parameters. Bak, Bruhn and Rastrup-Andersen find that the

TABLE II

SYMMETRIC TOP MOLECULES

Formula*	Experimental Results†	References
ND_3	measured inversion spectrum near 1,590 Mc.	(30)
AsF_3	$B_0 = 5{,}878.971 \pm .002$ Mc. also fine structure	(8)
$HGeCl_3$	from Ge and Cl isotopes: Ge–Cl = 2.114 ± .001 Å, Ge–H = 1.55 ± .04 Å, ∠ClGeCl = 108° 17′ ± 12′	(31)
$HSiCl_3$	from Cl isotopes: Si–Cl = 2.021 ± .002 Å, Si–H = 1.47 Å (assumed), ∠ClSiCl = 109° 22′ ± 15′	(32)
H_3SiF	from Si and H isotopes: Si–F = 1.594 ± .004 Å, Si–H = 1.46 ± .02 Å, ∠FSiH = 109° 40′ ± 20′	(33)
H_3SiCl	from Si and H isotopes: Si–Cl = 2.050 ± .001 Å, Si–H = 1.44 ± .01 Å, ∠ClSiH = 108° 20′ ± 1′	(34)
H_3SiI	$B_0 = 3{,}215.6$ Mc., assume H_3Si structure and obtain Si–I = 2.433 Å	(35)
CH_3SiCl_3	$B_0 = 1{,}769.836 \pm .025$ Mc.	(32)
$(CH_3)_3CF$	$B_0 = 4{,}712.45$ Mc.	(36)
$(CH_3)_2SiCl$	$B_0 = 2{,}197.441 \pm .038$ Mc.	(32)
CH_3CCCCH	$B_0 = 2{,}035.73$ Mc., $D_{JK} = 20.0$ kc.	(37)
$C_8H_{13}Cl$	$B_0 = 1{,}090.90 \pm .02$ Mc.	(38)
$C_8H_{13}Br$	$B_0 = 725.9 \pm .2$ Mc.	(38)

* Unless specified, data are given for molecular species containing the most abundant naturally occurring isotopes.

† For quadrupole data see Table IV.

change in bond distance is not too great, and the data for H_3SiF can be combined to yield the three comparatively accurate structural parameters given in Table II.

The compounds $C_8H_{13}Br$ and $C_8H_{13}Cl$ were found by Nethercot & Javan (38) to be symmetric tops. This indicates that they have threefold axes of symmetry and are respectively, 1-bromo and 1-chloro bicyclo (2,2,2) octane.

Asymmetric top molecules.—The structure of ozone has been a long standing problem. Some spectroscopic work has assigned an acute angle to the molecule and others an obtuse angle. Electron diffraction has assigned the molecule a structure of an isosceles triangle with an included angle of about 130°. A structure of this type for ozone makes it an asymmetric top with two structural parameters. From the microwave spectrum of an asymmetric top one can establish three moments of inertia. It is then possible, for ozone, to determine a complete structure from only one isotopic species. Hughes (39) determined the moments of inertia of five isotopic species of ozone. From these data he was able to calculate 15 values for the O–O–O angle which ranged from 116° 25′ to 117° 2′. The corresponding values for the two equal O–O distances went from 1.2747 Å to 1.2794 Å. Zero-point vibration is the source of this variation in the effective bond distance and angle. Trambarulo *et al.* (40)

measured some of the lower J valued rotational lines for ozone and their structural parameters are given in Table III.

TABLE III

ASYMMETRIC TOP MOLECULES

Formula*	Experimental Results†	References
O_3	$\angle O\text{-}O\text{-}O = 116° 49' \pm 30'$, $O\text{-}O = 1.278 \pm .003$ Å	(39, 40)
H_2S	$\angle HSH = 92° 6'$, $H\text{-}S = 1.3226$ Å	(3)
HDO	Some new lines, large centrifugal distortions	(7, 14, 41, 42)
HNCS	From H, N and S isotopes: $C\text{-}S = 1.561$ Å, $C\text{-}N = 1.216$ Å $N\text{-}H = 1.013$ Å, $N\text{-}D = 1.003$ Å, $\angle CNH = 130° 15'$, $\angle CND = 132° 16'$	(15)
ClF_3	Planar and "T" shaped, from Cl isotopes: Cl–F (two) = 1.698 Å, C–F (one) = 1.598 Å, $\angle FClF = 87° 29' \pm 3°$	(43)
Cl_2CO	From Cl isotopes: $C\text{-}Cl = 1.746 \pm .004$ Å, $C\text{-}O = 1.166 \pm .002$ Å, $ClCCl = 111.3 \pm .1°$	(44)
PH_2D	$P\text{-}H(D) = 1.4177$ Å, $\angle HPH(D) = 93° 21.6'$	(13)
PD_2H	$P\text{-}D(H) = 1.4116$ Å, $\angle DPD(H) = 93° 15.4'$	(13)
$ClFCH_2$	From Cl isotopes: $\angle HCH = 111° 56'$ (assumed), $C\text{-}H = 1.078$ Å, $C\text{-}Cl = 1.759$ Å, $C\text{-}F = 1.378$ Å, $\angle ClCF = 110° 1'$, $\theta = 125° 41'$	(45)
CH_3OH	From C and O isotopes: $O\text{-}H = 0.937$ Å, $C\text{-}O = 1.434$ Å, $\angle COH = 105° 56'$, $\angle HCH = 109° 30'$, $C\text{-}H = 1.093$ (assumed), $a = 0.079$ Å, Barrier = 374.8 $cm.^{-1}$	(46)
$(CH_2)_2NH$	(Ethylenimine) not C_{2v} symmetry, $A_0 = 6{,}039.13$ Mc., $B_0 = 5{,}804.70$ Mc. $C_0 = 2{,}959.25$ Mc.	(47, 48, 49)
$(CH)_5N$	(Pyridine) planar C_{2v}, $A_0 = 6{,}039.13$ Mc. $B_0 = 5{,}804.70$ Mc., $C_0 = 2{,}959.25$ Mc.	(50, 51)

* Unless specified, data are given for the molecular species containing the most abundant naturally occurring isotopes.

† For quadrupole data see Table IV.

Chlorine trifluoride has also proved to have a very interesting structure. The three fluorine atoms in the molecule are not equivalent and the molecular structure is very similar to a slightly distorted "T." The chlorine atom occupies the intersection of the arms and stem of a "T," the arms are bent down very slightly and the two equal arms are both longer than the stem. The exact dimensions are the work of Smith (43) and are given in Table III. If a molecule were planar and rigid, two of its moments of inertia should add to give the third. In the case of ClF_3 the quantity $I_c - (I_a + I_b)$ is less than 0.1 per cent of I_c. This discrepancy is easily accounted for by zero-point vibrations and ClF_3 is planar.

Methyl alcohol is the first asymmetric top molecule with internal rotation to be investigated by microwaves. The latest report on this molecule is by Ivash & Dennison (46) and their results are given in Table III. The structural parameters are based upon the spectra of $C^{12}H_3O^{16}H$, $C^{13}H_3O^{16}H$ and $C^{12}H_3O^{18}H$. From these data Ivash and Dennison were able to evaluate the moment of inertia of the methyl group about its own symmetry axis. Since this value was very close to the corresponding one for methane, a C–H distance equal to that in methane was assumed. The potential barrier to internal rotation was taken to have the form $V = H(1-\cos 3\phi)$, where ϕ is the angle of rotation of the OH group with respect to the CH_3 group. The value of the barrier, H, was determined to be 374.8 cm.$^{-1}$. Ivash and Dennison varied each of the four experimental frequencies that they used to determine the barrier by 100 Mc. (five-thousand times the experimental errors) and obtained only a maximum variation of 0.3 cm.$^{-1}$ in the barrier. Apparently further accuracy in the determination of the methyl alcohol parameters is limited either by higher order potential terms or by other types of rotation-vibration interaction. The small distance a reported by Ivash and Dennison is the displacement of the oxygen atom from the symmetry axis of the methyl group.

Only a single isotopic species of the molecules ethylenimine and pyridine have been examined. From these data it has been possible to establish the symmetry of the molecules but not the complete structures. In the case of ethylenimine, components of the dipole moment along both the b and c axes have been measured. These data together with intensity measurements prove that the molecule does not have C_{2v} symmetry. The moments of inertia determined by McCulloch & Pallow (50) for pyridine show that it is planar. Their measured intensities are also consistent with an assignment of C_{2v} symmetry.

Nuclear quadrupole interaction.—The interaction of nuclear quadrupole forces with molecular rotation has proved to be both an aid and a hindrance. It is a hindrance because in the case of many molecules this interaction leads to a resolvable fine structure. This fine structure reduces the intensity of the individual absorption lines and interferes with the application of the Stark effect for J value assignments. It is an aid, on the other hand, for once the quadrupole coupling constants are evaluated they can serve as a key to the electronic structure of a molecule.

Quadrupole coupling constants are a product of a nuclear quadrupole moment and a gradient of a molecular electric field. The sign of the quadrupole moment may be either positive or negative, e.g., Cl^{35} negative, D positive; and the nature of the electric field gradient depends upon the electronic structure of a molecule and the direction in which the gradient is measured. For linear and symmetric top molecules it is only necessary to specify the electric field gradient along the molecular symmetry axis, while in the case of asymmetric tops the directions of the three principal inertial axes are used. Townes & Dailey (52) have shown that the quadrupole coupling constants for a given nucleus in series of compounds can be used to determine the nature of the chemical bonding in those compounds. For exam-

ple, the coupling constant given in Table IV for Cl^{35} in D_3SiCl is less negative than that observed in H_3CCl (−75.3 Mc.). This indicates that the bonding of the Cl atom in D_3SiCl has more ionic character than that in H_3CCl. At the same time the coupling constant for H_3SiCl is −40.0 Mc. This same small difference upon isotopic substitution has also been observed for D_3CCl and H_3CCl. It indicates an interaction between vibration and the molecular electric field gradient.

TABLE IV

NUCLEAR QUADRUPOLE COUPLING CONSTANTS

Nucleus	Molecule	χ_{aa}*	χ_{bb}	χ_{cc}	Reference
As^{75}	AsF_3	−236.230 ± .050			(8)
Cl^{35}	D_3SiCl	−39.4			(34)
Cl^{35}	ClF_3	−81.25	−64.67	146.92	(43)
Cl^{35}	Cl_2CO	−37.20 ± .05	10.13 ± .05	27.07 ± .1	(44)
Cl^{35}	$ClFCH_2$	−52.2 ± 1	38.8 ± 1	13.4 ± .1	(45)
D	DCCCl	+0.175 ± .02			(6)
D	DCN	±0.30 ± .15			(6)
I^{127}	DI	−1805 ± 5			(2)
I^{127}	H_3SiI	−1240 ± 30			(35)
S^{33}	H_2S	−32	−8	+40	(13)
S^{33}	HNCS	−27.5 ± 0.8			(15)

* $\chi_{zz} = eQ\langle \partial^2 V/\partial z^2 \rangle_{av}$, for prolate symmetric tops χ_{aa} is usually designated eqQ and $\chi_{bb} = \chi_{cc} = -\frac{1}{2}\chi_{aa}$, all values given in Mc.

The HSH angle that has been found for H_2S is almost 90°. This fact has been taken in the past to indicate a fairly pure p bond. If such were the case the quadrupole coupling constants along the principal axes in the plane of the molecule for S^{33} should be equal. It can be seen in Table IV that χ_{aa} and χ_{bb} are far from being equal. Burrus & Gordy (3) have taken this difference as a measure of d hybridization in H_2S. Their supposition may be correct, for it does seem clear that the bonding is not pure p despite the near 90° angle.

The quadrupole moment of deuterium is only one twenty-fifth that of Cl^{35}. In addition, the usual bonds of hydrogen are mixtures of ionic and s covalent bonds, neither of which will contribute to quadrupole coupling. Despite these difficulties the coupling constants for deuterium in DCN and DCCCl have been measured. In the case of DCCCl the sign of the coupling constant indicates some π-character for the C–D bond. The existence of π-character appears to be consistent with the short (1.05 Å) C–H bond in HCCCl.

In asymmetric top molecules the principal inertial axes often do not coincide with any of the bonds in the molecule. In these cases the coupling constants can not be used for bond discussions unless they can be referred to bond axes. If the off-diagonal elements χ_{ab}, χ_{ac}, and χ_{bc} were known, the

procedure would be simple and rigorous. However, none of these off-diagonal elements have been determined and another method must be used. The most common procedure is to assume that the off-diagonal elements of χ will be equal to zero for axes corresponding to bond axes. If this assumption is made then the coupling constants of the bond axes can be calculated. Robinson (44) has done this for the Cl_2CO data and he finds that $\chi_{bond} = -78.7$ Mc. In addition, he finds that the two coupling constants perpendicular to the bond are not equal. The most ready explanation for this fact is that appreciable π-bonding exists. This fact has also been noted by Muller (45) for $ClFCH_2$ and he estimates 7 per cent π-character for the C–Cl bond.

The remarkable molecule ClF_3 does have the inertial and bonding axes almost coincident, but there are three Cl–F bonds contributing to the quadrupole coupling constants. An interesting calculation can be made for this molecule if pure p bonding is assumed for the central chlorine atom. In this model two electrons are placed in the p orbitals of the chlorine atom which are perpendicular to the plane of the molecule. The observed coupling constants χ_{aa} and χ_{bb} can then be combined with the known value of 110 Mc. for the coupling constant of a chlorine p electron. The result of this calculation is that the chlorine atom is left with only 1.3 additional p electrons. A total of 3.3 p electrons will produce a formal charge of $+1.7$ on the chlorine atom. Such a large positive charge on a chlorine atom is not completely unexpected in a compound containing three strongly electronegative fluorine atoms.

Nuclear magnetic dipole interaction.—Miller, Townes & Kotani (27) have shown that nuclear magnetic dipole coupling constants can also be used to determine the nature of a chemical bond. For the oxygen molecule they have been able to use the two coupling constants obtained from the spectrum of $O^{16}O^{17}$. These coupling constants depend upon the asymmetry of the electronic distribution in a molecule in a manner very similar to electric quadrupole interaction. Using the experimentally determined asymmetry, Miller, Townes, and Kotani have shown that the unpaired electrons in oxygen, in agreement with molecular orbital theory, are in $p\pi$ rather than $p\sigma$ orbitals.

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EXPERIMENTAL MOLECULAR STRUCTURE[1]

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This review of the year's work on molecular structure is concerned primarily with investigations which have led to values of interatomic distances. In addition, some attention is given to results concerned with the question of internal rotation.

A survey of the year's literature reveals an increase in the number of molecules for which very accurate values of interatomic distances are available. The attainment of such results has been aided by more widespread use of the sector technique in electron diffraction, by resolution of rotational Raman spectra, and by further use of microwave spectroscopy.

This report will not usually be concerned with the details of spectroscopic or x-ray methods since these subjects are discussed in other chapters in this volume. More detailed consideration will be given to the electron diffraction methods but molecules studied by x-ray and spectroscopic methods will be mentioned, especially where the results can be compared with those obtained by electron diffraction.

One book and one review article which appeared during the year should be called to the attention of scientists interested in the determination of molecular structures. The book, *Microwave Spectroscopy*, (1) by Gordy, Smith & Trambarulo deals with many aspects of this important branch of spectroscopy. The review article (2) by Jeffrey & Cruickshank, covers modern methods of x-ray crystal analyses of molecular structures and their accuracy.

Theory and Practice of Electron Diffraction by Gases

Perhaps the most unusual results of the year are those of Hedberg (3) who has been working in Oslo with Hassel and Bastiansen and has obtained sectored electron diffraction patterns of cyclooctatetraene which extend to $s=60$ ($q=191$). Since many diffraction results are based on data which do not extend beyond $s=25$ or 30 and the usual limit obtained in the past is about $s=35$, this would seem to offer the possibility of obtaining almost twice as much usable diffraction data, and such data, properly interpreted, could be extremely helpful in determining molecular parameters, including vibration factors. This report of such extensive patterns has been received with a certain amount of scepticism by electron diffraction workers in this country and it might be well to mention that diffraction patterns of benzene extending to about $s=50$ have been obtained at the California Institute of Technology (4); these photographs were taken without a rotating sector and could not, therefore, be due to sector imperfections.

[1] The survey of the literature pertaining to this review was concluded in January, 1954.

Every active electron diffraction laboratory in this country is either using or constructing equipment which incorporates a rotating sector. As is indicated in the results reported below, the quantitative intensities from sectored photographs permit much more accurate determinations of interatomic distances than have been obtained by the visual method. In particular, as new sector results are obtained, comparisons between bond distances in similar compounds should be more meaningful; frequently in the past the difference between a given bond distance in two similar molecules has been of the same order of magnitude as the estimated uncertainties, thus making it impossible to state with reasonable certainty that one distance is different from another.

One of the problems which arises in the recording and measurement of quantitative intensities is that of calibration of photographic plates; this problem has been discussed by Bartell & Brockway (5, 6) and by Karle & Karle (7).

The important discovery by Schomaker & Glauber (8) of the failure of the Born approximation was discussed in last year's review (9). More detailed treatments have now been published by Glauber & Schomaker (10) and by Hoerni & Ibers (11). It has also been pointed out that the atomic phase shifts discussed by Schomaker and Glauber must be taken into account in the calculation of vibrational amplitudes, even for light atoms [Bartell & Brockway (12)].

Bartell & Brockway (13) have used electron diffraction to investigate the electron distribution in atoms. Their experiments on argon gave diffraction patterns extending to $s=44$; analysis of these patterns gave an electron distribution which resolved the K, L and M shells and agreed well with the Hartree distribution.

An approximate method for calculating mean square amplitudes of vibration of atoms in molecules has been proposed by Morino *et al.* (14). The conclusions indicate that, provided some allowance be made for the errors of the mean amplitudes, a value can be assigned to the mean amplitude of a given pair of atoms, without referring to the structure of the remainder of the molecule. Numerical values have been given for various atom pairs and the usefulness of these in electron diffraction investigation has been indicated. In addition, Decius (15) has called attention to the high temperature or classical limit of the relations developed earlier by Morino *et al.* (16).

Bru (17, 18, 19) and his co-workers have published three interesting articles on the optical analogies between the diffraction of light and the diffraction of electrons by gaseous molecules. In the second and third of these papers (18, 19) Eller's optical machine has been applied to the determination of structure by a corrrelation procedure.

Electron diffraction workers are awaiting with interest the publication of the details of analysis of patterns extending to $s=60$ (3), and also the publication of the procedure employed by Brockway and his co-workers, whose results are discussed in the next section.

Structural Results

Halocarbons.—Brockway, Thornton & Bartell (20) have employed a new electron diffraction apparatus incorporating a rotating sector to reinvestigate the molecular parameters of the four fluoromethanes. For methyl fluoride they obtained C—F = 1.391 ±0.005 Å with C—H = 1.095 ±0.010 Å and ∠HCH = 109 ½ ±2°. The first of these results is in excellent agreement with the previous visual result of Schomaker & Stevenson (21) who reported C—F = 1.39 Å, but the accuracy of the new determination is much greater. The new results are also close to the parameters of 1.385 Å, 1.109 Å and 111°0′ obtained by Gilliam, Edwards & Gordy (22) from the microwave spectrum. For difluoromethane the new sector values (20) are C—F = 1.360 ±0.005 Å and ∠FCF = 108.2 ±0.8°; these are to be compared with the recent visual results of Hamilton & Hedberg (23) who reported $1.35_7 \pm 0.01_7$ and 107.5 ±1.5° and with the microwave work of Lide (24) who obtained 1.358 ±0.001 Å and 108°17′ ±6′. All of these results on difluoromethane confirm the value of 1.36 ±0.02 Å obtained by Brockway in 1937 (25) but suggest that the infrared spectroscopic result of 1.32 Å [Stewart & Nielsen (26)] is not correct. The sector results (20) for fluoroform are C—F = 1.334 ±0.005 Å and ∠FCF = 108.5 ±0.5°; these are in excellent agreement with the recent microwave values of 1.332 Å and 108°48′ obtained by Ghosh, Trambarulo & Gordy (27). The original diffraction results (28) on carbon tetrafluoride gave C—F = 1.36 ±0.02 Å which seemed surprising in light of the shorter distances in fluoroform and difluoromethane. A reinvestigation of CF_4 by Hoffman & Livingston (29), using the visual method, gave $C—F = 1.31_7 \pm .015$ Å and a sector investigation by Brockway, Thornton & Bartell (20) gave 1.323 ±0.005 Å, in close agreement with the visual result. It is interesting to note that a neutron diffraction study (30) of CF_4 vapor gave 1.33 Å which is apparently more nearly correct than were the distances obtained in the early electron diffraction studies (28). The new results for CF_4 also would seem to indicate definitely that there is decrease in the C—F distance as one progresses down the series from CH_3F to CF_4. It is gratifying to have, at last, what most certainly are reliable results on this interesting series of compounds on which so many conflicting results have been obtained in the past.

Brockway, Thornton & Bartell (20) have also reinvestigated methyl chloride and trifluoromethyl chloride by the sector method in order to determine the effect of the fluorine atoms on the C—Cl bond distance. For CH_3Cl they obtained C—Cl = 1.784 ±0.002 Å which compares well with the microwave value of 1.781 ±0.005 Å (31, 32). For CF_3Cl, the new sector results are C—Cl = 1.751 ±0.004 Å and C—F = 1.328 ±0.002 Å with ∠FCF = 108.6 ±0.3°; the microwave data of Coles & Hughes (33) have been shown by Sheridan & Gordy (34) to yield values of 1.740 ±0.018 Å and 1.328∓ 0.005 Å if the FCF angle is assumed to be 108 ±1°. In this case the electron diffraction results are apparently somewhat more accurate but either result leads to the conclusion that the C—Cl distance is significantly shorter in CF_3Cl than in CH_3Cl. It is of interest to note that Burbank (35) has deter-

mined the structure of solid CH_3Cl at $-125°$ C.; he obtained 1.80_5 Å for the C—Cl distance but the difference between this value and the distance in the gaseous molecule may not be significant since it might be due to random errors in the x-ray experiment.

One additional fluorine derivative of methane, CH_2ClF, has been studied by microwave spectroscopy by Muller (36) who obtained a C—Cl distance of 1.759 ± 0.003 Å and a C—F distance of 1.378 ± 0.006 Å. It is interesting to note that the C—Cl distance in this compound is less than in CH_3Cl and that the C—F distance is close to the C—F distance in CH_3F.

Using the quantitative electron diffraction methods developed by J. Karle, I. Karle & Hauptman (37, 37a, 38), interatomic distances in CCl_2CCl_2 have been determined by Swick (39). The results are C—Cl = 1.74 ± 0.01 Å, C—C = $1.57 + a \pm 0.06$ Å, $\angle CCl = 109°40' - 24a° \pm 30'$ where $a = l - 0.06$ and $l = \langle l^2 \rangle_{av.}^{1/2}$ for the 1, 1′ Cl atoms is 0.06 {+0.04 or −0.07}. These values differ significantly from those obtained in previous electron diffraction studies (40, 41) and indicate that the C—Cl distance is less in this compound than in $CHCl_3$ where it has been reported to lie between 1.760 and 1.770 Å (27, 28, 42). These C—Cl distances can also be compared with the values $1.77_6 \pm 0.02$ Å, $1.77_6 \pm 0.02$ Å and 1.80 ± 0.04 Å in CH_3CCl_3, $(CH_3)_2CCl_2$ and $(CH_3)_3CCl$, respectively, obtained by the visual method by Coutts & Livingston (43). Tertiary butyl chloride has also been reinvestigated by Bastiansen & Smedvik (44) using the sector method; their value for C—Cl is 1.80 ± 0.01 Å. The latter authors also studied $(CH_3)_3CF$ (44) and obtained C—F = 1.38 ± 0.02 Å with $\angle CCF = 108 \pm 1.5°$; a combination of the electron diffraction and microwave data on this compound (45) led to C—F = 1.37 ± 0.01 Å and $\angle CCF = 108\ \frac{1}{2}°$ with C—C assumed to be 1.54 Å. The above mentioned results on CH_3CCl_3, $(CH_3)_2CCl_2$ and $(CH_3)_3CCl$ all indicate C—C distances between 1.50 Å and 1.58 Å, and Schomaker (28) has found this distance to be 1.54 ± 0.02 Å in CH_3CH_2Cl. It is therefore surprising, as noted in last year's review (9), that the C—C distance in ClH_2CCH_2Cl was found to be 1.49 ± 0.03 Å by Ainsworth & Karle (46) in a sector study of this compound. But exactly this same distance has been found by Reed & Lipscomb (47) who investigated solid CH_2ClCH_2Cl at $-140°$ C. by x-ray diffraction.

Fluorobenzene has been investigated by microwave spectroscopy [Erlandsson (48)] and reinvestigated by the visual method of electron diffraction [Yuzawa & Yamaha (49)]. The former work led to C—C = 1.392 Å and C—F = 1.348 Å while the latter gave C—C = 1.39 ± 0.02 Å with C—F = 1.30 ± 0.03 Å. It is not clear just how the choice was made among various models in the diffraction study nor is it clear why both the C—C and C—F distances were varied in calculating theoretical intensity curves. It is true, however, that the C—F distance of 1.30 Å agrees fairly well with the value of 1.31 Å obtained by the sector method and reported by Hassel & Viervoll (50). It is hoped that more work will be done on this compound in order to resolve the discrepancy between the diffraction and spectroscopic results. Yuzama & Yamaha (49) have also investigated bromobenzene; the comments regarding their methods on fluorobenzene would seem to apply here also.

Oosaka & Akimoto (51) have studied the molecular structures of *o*- and *p*-fluorochlorobenzene and *p*-fluorobromobenzene by the visual electron diffraction method. They report C—Cl = 1.69 ±0.02 Å and 1.68 ±0.02 Å for the first and second compounds, respectively, and C—Br = 1.87 ±0.02 Å for the third; in all cases C—F is given as 1.30 ±0.03 Å with the C—C distance very nearly 1.40 Å. A careful examination of their procedure and of their published curves suggests that the estimated uncertainties should be larger and that more models should have been considered, particularly some with longer C—F distances.

The microwave spectrum of 1-bromo- and 1-chloro bicyclo [2,2,2] octane has been studied by Nethercot & Javan (52). With certain assumptions as to the shapes of the molecules they arrive at C—C = 1.545 ±0.004 Å for both molecules.

Other organic molecules.—Formic acid (monomer), a molecule whose structure was the source of controversy in the past, has been reinvestigated by the sector method by I. Karle (53). The new results are C—O = 1.36 ±.01 Å, C—O = 1.23 ±0.01 Å and ∠OCO = 122.4 ±1°; these distances are in agreement with those obtained visually by Schomaker & O'Gorman (54) when one takes into account the larger estimated uncertainties reported in the latter investigation. The sector study has also yielded values for the mean amplitudes of vibration of the atoms. Holtzberg, Post & Fankuchen (55) have investigated formic acid crystals at −50°C. by x-ray diffraction and report C—O = 1.26 ±0.03 Å; C=O = 1.23 ±0.03 Å with ∠OCO = 123 ±1°; these results indicate that there is a marked change in the long C—O distance when condensation from the vapor to the solid occurs. Two preliminary analyses of the microwave spectrum of formic acic have also appeared (56, 57) and one of these reports (57) deals also with acetic acid.

The structure of phosgene has been investigated, both in the vapor and solid phases. From the microwave spectrum of the gaseous molecules, Robinson (58) obtained C—O = 1.166 ±0.002 Å, C—Cl = 1.746 ±0.004 Å and ∠ClCCl = 111.3 ±0.1°. An x-ray study of the crystal by Zaslow, Atoji & Lipscomb (59) yielded C—O = 1.15 ±0.02 Å, C—Cl = 1.74 ±0.02 Å and ∠ClCCl = 111.0 ±1.5°.

Ivash & Dennison (60) have carried out a detailed analysis of the microwave spectrum of methyl alcohol and have obtained values for the molecular parameters which are more accurate than the earlier values (61). It was not possible to determine the C—H distance with any accuracy and it was, therefore, assumed to be the same as in methane (1.093 Å); values of the other parameters were determined as C—O = 1.434 Å, ∠COH = 105°56′ and ∠HCH = 109°30′. As reported earlier (61), the symmetry axis of the methyl group passes between the hydrogen and oxygen atoms; the new analysis indicates that this axis is 0.079 Å from the oxygen atom. The potential barrier was found to be 1071 cal./mole, assuming a sinusoidal potential. In addition, an x-ray investigation of crystalline methyl alcohol by Dreyfus-Alain & Viallard (62) gave a C—O distance of 1.42 Å which is virtually the same as that obtained for the gaseous molecule. Finally, the influence of the torsional

oscillations on the cross section of CH_3OH for neutrons has been discussed by Janik (63).

Methyl cyanide has been reinvestigated by the visual electron diffraction method by Badgley, Danford & Livingston (64) in an attempt to resolve the discrepancy between the microwave (65) and early electron diffraction results (66) on this compound. The new diffraction data, which extended to larger scattering angles than did the older data, gave C—C = $1.46_5 \pm 0.02$ Å, C—N = $1.15_5 \pm 0.03$ Å, and C—H = 1.07 Å; these values are in excellent agreement with the microwave results.

Kimura & Aoki (67) have investigated the structures of acetamide and *N*-methylacetamide by the visual electron diffraction method. For acetamide they report C=O = 1.21 ± 0.02 Å, C—N = 1.36 ± 0.02 Å, C—C = 1.53 ± 0.03 Å, $\angle NCO = 125 \pm 3°$ and $\angle CCO = 122 \pm 4°$; they compare these values with those obtained by Senti & Harker (68) for crystalline acetamide which are 1.28 ± 0.05 Å, 1.38 ± 0.05 Å, 1.51 ± 0.05 Å, $122 \pm 5°$ and $129 \pm 5°$. Although Kimura and Aoki conclude that the molecule has different parameters in the gas and solid phases, their curve calculated for a model corresponding to Senti and Harker's structure has been shown to be completely wrong (69). Considering, in addition, the large uncertainties in the crystal parameters, it cannot be regarded as certain that the solid and gaseous molecules have different structures. No quantitative comparisons of q values are given in the study of gaseous acetamide and it is difficult to assess the validity of the results, particularly for a problem involving 5 major parameters. The case of *N*-methylacetamide is even more difficult but Kimura and Aoki have concluded that it has a *trans* configuration.

Igarashi (70) has reinvestigated ethylene oxide by electron diffraction; his results are consistent with the microwave results on this compound (71) but are not sufficiently complete to be regarded as independent confirmation for the structure obtained by microwave spectroscopy.

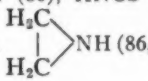
Aoki (72) has investigated the structures of dimethoxymethane and the trimer of acetaldehyde (paraldehyde). In the former, a C—O distance of 1.42 ± 0.02 Å is obtained and the visual intensity curve agrees with a curve corresponding to the configuration which has been suggested as the most stable one on the basis of dipole-moment data (73). For paraldehyde it is found that no single form gives agreement with the diffraction data and therefore it is concluded that paraldehyde is a mixture of two or more coexisting isomers.

A note by Stoicheff (74) describes the resolution of the rotational structure in the Raman spectrum of benzene; the rather novel results led to a value of B_0 from which the C—C separation was calculated as 1.396 to 1.401 Å assuming a planar, hexagonal ring with C—H = 1.06 to 1.09 Å. Extension of this technique may permit the spectroscopic determination of interatomic distances for molecules with large moments of inertia but which, due to the lack of a permanent dipole moment, will not absorb in the microwave region. The new Raman results on benzene agree well with a recent sector electron diffraction study by I. Karle (75) but there is apparently a real difference be-

tween the distances in the gaseous and crystalline molecules. The distance in the solid has been determined by Cox & Smith who found C—C (average) = 1.378 Å (76).

The unusual diffraction patterns of cyclooctatetraene mentioned earlier have been analyzed (3). The D_{2d} tub structure is confirmed with C—C = 1.462 Å, C=C = 1.334 Å, ∠C=C—C = 126.5°, C—H = 1.092 Å and ∠C=C—H = 119°; also the vibration factors have been determined. These distances agree well with those obtained several years ago in a visual study by Hedberg & Schomaker (77) but, unfortunately, there is a discrepancy between these new values and those obtained by I. Karle in another sector study (75). Further work is apparently necessary to resolve the discrepancy between these results.

Kimura & Kubo (78) have reinvestigated the structure of tropolone, using the visual correlation procedure with some guidance from a radial distribution curve. Based on the assumption of a regular heptagonal ring with C—C = 1.39 Å, they conclude that the molecule has two different C—O distances of 1.34 and 1.26 Å.

A number of additional organic molecules have been studied by microwave or infrared spectroscopy. Since these subjects are dealt with in detail in other chapters, only a mention of these compounds will be made here. The molecules studied include the CS radical (79), HCN (80), HNCS (81), CH_4 (82, 82a), $C(NO_2)_4$ (83), CH_3NH_2 (84), CH_2CO (85),  NH (86, 86a, 86b), and pyridine (87, 88).

Silicon and germanium compounds.—The structures of a rather large number of silicon and germanium compounds have been studied during the year. The following silicon compounds were investigated by microwave spectroscopy: $SiHCl_3$ (89), SiH_3Cl (90), SiH_3F (91), SiH_3I (92), $(CH_3)_3SiCl$ (89), and CH_3SiCl_3 (89). It is interesting that one obtains here an effect similar to that found in the fluoromethanes—the silicon-halogen distances are shorter in $SiHF_3$ (93) and $SiHCl_3$ than in SiH_3F and SiH_3Cl, respectively, as had been previously shown for the chlorine compounds by electron diffraction studies (28). The situation on $(CH_3)_3SiCl$ is not clear since the microwave results (89) are in apparent disagreement with the electron diffraction results (28); the former gave Si—Cl = 2.03 Å (assuming C—H = 1.093 and all angles tetrahedral) while the latter gave Si—Cl = 2.09 ±0.03 Å. The new results on CH_3SiCl_3 (89) are in agreement with a previous electron diffraction study (28).

Microwave spectroscopic studies of $GeHCl_3$ (94), GeH_3Cl (32), and GeF_3Cl (95) have led to Ge—Cl distances in these compounds of 2.114, 2.148, and 2.067 Å, respectively; these results again show an effect similar to that observed in the halogen derivatives of methane.

Iida, Yokoi & Yamasaki (96) have studied the structures of $C_2H_5SiCl_3$, $CH_2ClCH_2SiCl_3$, $CH_3CHClSiCl_3$, and $(SiCl_3)_2CH_2$ by electron diffraction. They reported Si—Cl = 2.00 Å, Si—C = 1.88 Å and ∠ClSiCl = 109 ½° for

all four compounds and estimated, for $CH_2CHClSiCl_3$, a potential barrier of about 3 kcal./mole hindering rotation about the Si—C axis. A preliminary report by Murata (97) on an electron diffraction investigation of vinyl- and dichlorovinyltrichlorosilane indicates that in the former the CH_2 group has a *cis* configuration to a chlorine atom on the $SiCl_3$ group while in the latter the Cl atoms in the dichlorovinyl are *trans* to each other. Yokoi & Yamasaki (98) have investigated the structures of hexamethylcyclotrisilazane ($[Si(CH_3)_2NH]_3$) and octamethylcyclotetrasilazane ($[Si(CH_3)_2NH]_4$). In the former compound they could not distinguish between boat and chair form models and found Si—N = 1.78± 0.03 Å, Si—C = 1.87±0.05 Å, ∠NSiN = 111±5° and ∠SiNSi = 117±4°with ∠CSiC assumed to be 110°. In the second compound, no detailed information on the shape of the ring could be obtained and no systematic survey of the parameter field was made. Even in the first compound, the well-known difficulties of such a many-parameter problem cause one to wonder if the results are significant since they were based on a fairly small number of calculated models.

Other inorganic molecules.—A few additional inorganic molecules have been studied by electron diffraction during the past year. Badgley & Livingston (64) reinvestigated the structure of phosphorus oxytrichloride because of a serious discrepancy between the earlier electron diffraction results (28) and more recent microwave results (99); the former were P—Cl = 2.02 ±0.03 Å, ∠ClPCl = 106 ±1° and P—O = 1.58 Å (assumed) while the latter results were 1.99 ±0.02 Å, 103.6 ±2° and 1.45 ±0.03 Å. The new diffraction results are P—Cl = 1.99_5 ±0.02 Å, ∠ClPCl = 103.5 ±1° and P—O = 1.45 ±0.05 Å and are thus seen to confirm the values obtained from the microwave spectrum. One wonders why the earlier diffraction results on this compound, as well as in other cases were apparently in error. Frequently, such errors have arisen because of a misinterpretation of the (visually-determined) shapes of certain features on the diffraction pattern. Particularly when the patterns did not extend to very large scattering angles, was it common practice to attempt to choose between models whose theoretical intensity curves differed only slightly; this can generally be avoided, even in the use of the sector method, by obtaining patterns which extend to greater s values. In the case of $POCl_3$, the new results are based on more extensive patterns and the interpretation of the seventh and eighth maxima differed in the two investigations.

Harvey & Bauer (100) have reported an interesting diffraction investigation of the molecular structure of disulfur decafluoride; their results were discussed in last year's review (9).

The group VI tetrahalides have been of unusual interest. Some time ago Stevenson & Schomaker (101) reported that tellurium tetrachloride did not have a regular tetrahedral structure. Lister & Sutton (102) presumably studied the structure of selenium tetrachloride vapor but were not aware that this gaseous compound is completely dissociated into $SeCl_2$ and Cl_2; recent calculations (103) have shown that curves calculated for mixtures of $SeCl_2$ and Cl_2 agree better with their diffraction data than did curves for either of the

models of $SeCl_4$ which they considered. This past year Bowen (104) has added another result to this group by determining the structure of selenium tetrafluoride. He found best agreement with a C_{2v} model having a distorted tetrahedral structure with two opposite FSeF angles at 120° and the remaining four FSeF angles at 104.5°. The Se—F distance was given as 1.765 ±0.025 Å and the uncertainty in the angles was estimated at ±10°. While these rather large uncertainties on the angles would appear barely to exclude the regular tetrahedral configuration, the authors feel that this structure has been eliminated.

Ibers & Schomaker (105) have reinvestigated the structure of oyxgen fluoride (OF_2). The electron diffraction data alone led to a bond angle of 103.8 ±1.5° with O—F = 1.413 ±0.019 Å while a combination of the diffraction data with the spectroscopic rotational constants of Bernstein & Powling (106) gave 103.2° and 1.418 Å as most probable values. In this diffraction investigation, special attention was given to the problem of weighing the measured ring diameters; the suggested procedure may be found useful by other workers in this field.

Several additional inorganic molecules have been studied by microwave or infrared spectroscopy but only a few will be dealt with in any detail here. Among the most interesting results are those on chlorine trifluoride which has been investigated in the gaseous phase by microwave spectroscopy and in the solid phase by x-ray diffraction. The microwave results of Smith (107) yield a distorted *T* structure (C_{2v} symmetry) with one short (1.598 Å) and two long (1.698) ClF bonds and with an FCF angle (between bonds of different lengths) of 87°29′; the estimated uncertainties are given as 0.005 Å. The x-ray diffraction investigation by Burbank & Bensey (108) also indicated a distorted planar *T* structure but the short bond distance is 1.621 Å and the two long distances are 1.716 Å with ∠FClF = 86°59′; the uncertainties are estimated to be less than 0.01 Å. The authors emphasize that there is no doubt that the dimensions of the gaseous and solid molecules are different. In addition, this seems to be the first case of a molecule of the type XY_3 (with the three Y atoms attached to the X atom) which does not have either C_{3v} or D_{3h} symmetry.

The structure of ozone has been a considerable source of controversy in the past. Agreement on the shape of the molecule was finally reached in favor of the obtuse-angled triangle model, which was the only shape consistent with the electron diffraction patterns. The results of two microwave investigations now indicate a bond angle of about 116–117° [Trambarulo *et al.* (109) and Hughes (110)]. This angle is about ten degrees less than that obtained in the earlier electron diffraction investigation (111) but the O—O bond distances obtained by both methods are in essential agreement.

Additional work has been done on the gaseous alkali halides, both by microwave spectroscopy and by use of molecular beams. Using the former method to study NaCl, Stitch, Honig & Townes (112) have found r_e = 2.3606 ±0.0003 Å, a value which is significantly less than the electron diffraction result of 2.51 ±0.03 (113) but presumably much more accurate. A

possible explanation for the discrepancy between these results is the evidence found by Ochs, Cote & Kusch (114) for the existence of dimers of NaCl in the vapor state; this unusual result is based on the molecular beam magnetic resonance method. For KBr, Fabricand *et al.* (115) have used the molecular beam electrical resonance method to study the hyperfine structure of the first rotational state, which is split into 10 levels by the quadrupole interaction of K and Br: they obtained $r_e = 2.8207 \pm 0.0001$ Å. Microwave spectroscopic results were obtained by Honig, Stitch & Mandel (116) on CsF, CsCl, and CsBr; the internuclear distances, r_e, were given as 2.3453, 2.9062, and 3.0720 Å, respectively, with estimated uncertainties of 0.0001 Å in all cases. The agreement between these distances and those obtained in an early electron diffraction study (113) is not good; the electron diffraction values are 0.07 to 0.15 Å lower.

Other molecules studied by spectroscopy include NH_3 (117), N_2O (118), NO (119), PH_3 (120, 121), O_2 (122), H_2O (123, 124), H_2S (125), HCl (117), HBr (117), HI (119, 126).

Molecular Crystals

Interatomic distances and other structural information have been obtained for a number of molecules in the solid phase by x-ray diffraction. Several relatively small and simple molecules have been investigated and some of these have been mentioned in preceding sections where comparisons with recent work on the gaseous molecules was possible; additional molecules will be discussed here.

Lavine & Lipscomb (127) have determined the structures of B_5H_{11}. The interesting molecular geometry of this compound is shown in Figure 1 and

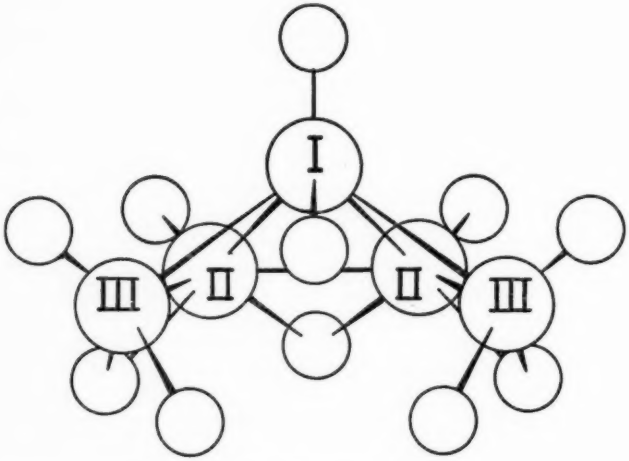


Fig. 1. The molecular structure of B_5H_{11}.

preliminary values of the interatomic distances are as folllws: $B_IB_{III} = 1.86_5 \pm 0.00_5$ Å, $B_{II}B_{III} = 1.75 \pm 0.02$ Å, $B_IB_{II} = 1.72 \pm 0.02$ Å, $B_{II}B_{II} = 1.77$ Å seven B—H = 1.07 ±0.04 Å, six B—H = 1.24 ±0.07 Å, one B—H = 1.00 Å and two B_{II}—H = 1.67 ±0.09 Å. A discussion of the relation of this structure to the structures of B_4H_{10}, B_5H_9 and $B_{10}H_{14}$ is also given (127). The structure of B_4H_{10} was discussed in one of last year's reviews (128) and three publications on this molecule have appeared, one dealing with the gaseous molecule (129) and the other two with the solid (130, 131).

An x-ray diffraction investigation of solid trimethylaluminum has been conducted by Lewis & Rundle (132). Although early electron diffraction data of this compound were interpreted on the basis of an ethane-like structure, a more recent electron diffraction study by Schomaker (133) and the present x-ray work confirm the bridge structure with D_{2h} symmetry. The latter investigation gave Al—C (bridge) = 2.24 Å, Al—C(exterior) = 1.99 Å, exterior ∠CAlC = 124° with the bridge ∠AlCAl = 70.°

It is interesting to compare the structure of molecules in the solid and gas phases. This is done in Table I for a number of recent results, including several cases discussed above. Of the molecules listed, it seems that only in the cases of formic acid, benzene, and chlorine trifluoride is there strong evidence for differences in interatomic distances.

Several more crystalline organic compounds have been the subject of x-ray diffraction studies. Oxamide has been found by Romers (140) to have the following interatomic distances: C—C = 1.49 Å, C—O = 1.25 Å, and C—N = 1.31 Å. Shahat (141) reports for maleic acid a C—C bond distance of 1.45 ±0.02 Å with C—C—C angles of 125 ±1°. In dicyanoacetylene, C≡N = 1.14 Å, C—C = 1.37 Å and C≡C = 1.19 Å [Hannan & Collin (142)]; it is interesting to note that this single bond distance is virtually the same as in cyanoacetylene, cyanogen, and diacetylene which seems to indicate that the addition of a third triple bond to the conjugated system has only a small effect on the structure. Dougill & Jeffrey (143) have found for dimethyl oxalate a planar *trans-trans* configuration. For dimethyltriacetylene, H_3C—C≡C—C≡C—C≡C—CH_3, Jeffrey & Rollett (144) reported the following distances: C—C(terminal) = 1.46_6 Å, C—C(middle) = 1.37_5 Å and C≡C = 1.19_9 Å. Cruickshank & Robertson (145) made theoretical and experimental determinations of the structure of naphthalene and anthracene; they find C—C bond distances varying from 1.365 to 1.436 Å, and also that the molecular orbital theory gives good agreement for the latter compound but not for the former. Donaldson & Robertson (146) have found that octamethylnaphthalene has a nonplanar structure; the methyl groups lie considerably out of the plane and the carbon rings themselves are probably not all in one plane. The same authors (147) have investigated the structure of ovalene (octabenzonaphthalene) and found that it has twelve distinct carbon-carbon bonds which vary in length from 1.355 to 1.438 Å. The structure of dimethyl glyoxime has been determined by Merritt & Lauterman (148) who found normal bond lengths except for the central C—C bond which they report as 1.44 Å.

Other molecules studied by x-ray diffraction include diethylsilane-diol

TABLE I

COMPARISONS OF INTERATOMIC DISTANCES*

Compound	Gas	Method† and Reference	Solid	Reference
CH_3Cl	C—Cl = 1.784 ± 0.002 1.781 ± 0.005	ED (20) M (31, 32)	1.80_5	(35)
CH_3NH_2	C—N = 1.47 ± 0.01	ED (28)	$1.48 \pm 0.01_4$	(136)
CH_3OH	C—O = 1.434	M (60)	1.42	(62)
HCOOH	C—O = 1.36 ± 0.01 C=O = 1.23 ± 0.01 ∠OCO = 122.4 ± 1°	ED (53)	1.26 ± 0.03 1.23 ± 0.01 123 ± 1°	(55)
$COCl_2$	C—O = 1.166 ± 0.002 C—Cl = 1.746 ± 0.004 ∠ClCCl = 111.3 ± 0.1°	M (58)	1.15 ± 0.02 1.74 ± 0.02 111.0 ± 1.5°	(59)
HC≡CH	C≡C = 1.205 ± 0.008	ED (137)	1.20	(138)
ClH_2CCH_2Cl	C—C = 1.49 ± 0.03	ED (46)	1.49 ± 0.03	(47)
$H_3C—C≡C—CH_3$	C—C = 1.47 ± 0.02	ED (66)	1.455	(139)
Benzene	C—C = 1.396—1.401 1.393	R (74) ED (75)	1.378	(76)
$Ni(CO)_4$	Ni—C = 1.82 ± 0.03 C—O = 1.15 ± 0.02	ED (135)	1.84 ± 0.03 1.15 ± 0.03	(134)
ClF_3	Cl—F = 1.598 ± 0.005 Cl—F′—1.698 ± 0.005 ∠FClF = 87°29′	M (107)	1.621 ± 0.01 1.716 ± 0.01 86°59′	(108)

* All distances are given in Å.

† ED = electron diffraction; M = microwave spectroscopy; R = Raman spectroscopy.

[Kakudo & Watase (149)], benzene iododichloride (Archer & van Schalkwyk (150)], α-thiopyridone [Penfold (151)], 3,3′-dichloro-4,4′ dihydroxydiphenylmethane [Whittaker (152)], diphenylene naphthacene [Bennett & Hanson (153)], dimethanesulphonyl disulfide [Sorum (154)], *trans* 1,4-chlorobromocyclohexane [Hassel & Vihovde (155)], cyclooctatetraenecarboxylic acid [Kinder & Shoemaker (156)], sulfamide [Mayer & Trueblood (157)], copper acetylacetonate [Rundle & Dahl (158)], and normal paraffin hydrocarbons

[Smith (159)]. It should also be noted that some x-ray diffraction studies published this year were included in last year's review by Lipscomb (128).

Internal Rotation and Rotation Isomerism

Considerable interest still exists in the problem of restricted internal rotation and the existence of rotational isomers; a number of interesting examples were reported in last year's review. During the past year several additional molecules have been studied from this point of view.

From an investigation of the infrared spectrum of CH_3CCl_3, Pitzer & Hollenberg (160) have determined not only the height but the shape of the potential barrier which hinders the internal rotation of the CCl_3 group with respect to the CH_3 group. The shape of the potential curve was found to be only very slightly different from the simple one-term cosine curve which has generally been applied to such problems. Interpretation of the spectrum on the basis of the simple curve gives a barrier of about 3.0 kcal./mole.

The energy differences between rotational isomers of 1,1-dichloroethane, 1,1-chlorobromoethane and 1,1-dibromoethane have been reported by Kuratani, Miyazawa & Mizushima (161). Their results indicate the energy difference between the *gauche* and *trans* forms is less in the liquid than in the vapor state.

The magnitude of the potential barrier in methyl alcohol has been mentioned above (60). Additional work on the spectrum and heat capacity of ethyl alcohol has been done by Barrow (162). He obtains best agreement between the observed and statistically calculated heat capacities and entropies with internal rotation barriers of 3.30 and 0.8 kcal./mole for the CH_3 and OH groups, respectively. These values agree with those suggested earlier (163).

An interesting case of rotation within a crystalline solid has been reported by Shimizu & McLachlan (164). They investigated crystalline trimethylamine sulfur trioxide by x-ray diffraction and concluded that the SO_3 groups rotate about the molecular axis while the $N(CH_3)_3$ groups rotate very little, if at all.

Rather surprising results have been obtained for the three molecules $ClH_2C{-}C{\equiv}C{-}CH_2Cl$, $F_3C{-}C{\equiv}C{-}CF_3$ and $H_3C{-}C{\equiv}C{-}CF_3$. In each case, evidence has been reported for restricted internal rotation. For the first molecule, Morino, Miyagawa & Wada (165) have observed an increase in dipole moment with increasing temperature and conclude that this is due to hindered internal rotation; their data are consistent with a potential barrier of 0.75 ± 0.20 kcal., assuming a simple one-cosine potential function. Although the dipole moments were determined in benzene and carbon tetrachloride solutions, almost identical values were obtained in both solvents.

In the case of $F_3C{-}C{\equiv}C{-}CF_3$, Miller & Bauman (166) have studied the infrared and Raman spectra. They observed no coincidences between the Raman and infrared frequencies and hence concluded that the molecule has D_{3d} symmetry which implies restricted rotation of the CF_3 groups. While such evidence is certainly consistent with the stated symmetry, it cannot be regarded as conclusive proof. The microwave spectrum of $F_3C{-}C{\equiv}C{-}CH_3$ has been shown by Bak, Hansen & Rastrup-Anderson (167) to consist of

groups of lines for each rotational transition; these closely spaced lines are taken as corresponding to the presence of torsionally excited levels. It should be noted that the hydrogen-halogen or halogen-halogen distances in these compounds is of the order of 5 Å and the cause of any restricted rotation raises an interesting question.

Ziomek *et al.* (168) have examined the Raman and infrared data for oxalyl chloride and concluded that the *trans* form very likely predominates to the virtual exclusion of any of the *cis* form at room temperature and above. This conclusion has been questioned by Kagarise (169) who has compared the infrared spectrum of liquid and solid oxalyl chloride; it does not appear possible to explain his data on the basis of a single molecular species of the *trans* form or on the basis of any single molecular species. In addition, the work of Saksena *et al.* (170, 171) on temperature-intensity effects was interpreted as indicating an energy difference of 2.8 kcal./mole between the *trans* and *cis* forms, the *trans* being more stable.

The thermodynamic properties and configuration of unsymmetrical dimethylhydrazine have been studied by Aston, Wood & Zolki (172). Agreement between the observed and calculated entropy is obtained with barriers of 3700 and 3000 cal./mole hindering the methyl and amino groups, respectively, provided an equimolar mixture of *d-gauche* and *l-gauche* (rather than *trans*) forms is assumed. Agreement can also be obtained with the same barrier but assuming 75 per cent *trans* and 25 per cent *d-gauche* and *l-gauche;* this mixture is considered unlikely in light of the fact that the *trans* form has been shown to exist only in negligible quantities at room temperature in the case of hydrazine, methyl hydrazine, and sym-dimethylhydrazine.

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ION EXCHANGE[1]

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Introduction

Developments in the fundamental aspects of ion exchange during the past year are characterized by marked refinements or "sharpening" of the theoretical and experimental approaches. Investigators in the ion exchange field are now drawing heavily on the theories and on the more precise and accurate experimental techniques employed both in the polyelectrolyte field and in the physical chemistry of electrolytic solutions. In the latter connection, the book by Harned & Owen (1) is indispensable. A gratifying amount of excellent data is now available on such topics as isopiestic measurements, self-diffusion and inter-diffusion coefficients, and conductance of ion exchange resins. Consequently, it is becoming possible to describe the internal phase of the ion exchange resins sufficiently well so that reasonably accurate deductions and calculations can begin to be made on equilibrium constants, activity coefficients of the internal resin phase constituents, hydration, and other properties described in this review. Additional work of a systematic nature relating to temperature effects and the ion exchange behavior of polyvalent electrolytes in particular is needed.

Ion exchange resins are of importance in physical chemistry not only in themselves but also because they can and are being used increasingly as a tool for the study of electrolytic solutions as was mentioned briefly in earlier reviews (2, 3). In this respect ion exchange resins have been used for the determination of properties such as: the composition and formation quotients of complex ions, the charge and state of an ion in solution, activity coefficients in mixed electrolytes, the approximate size of polymerized species, and for deductions concerning electronic configurations in the actinide elements. Particular attention is given in this review to the historical development of the use of ion exchanger as a physico-chemical tool.

Developments in ion exchange in inorganic and organic separations, biochemistry, water softening, and the like are generally not included here except to the extent that they contribute information of general value or reveal novel features of general applicability.

During the year a book on the use of ion exchangers in analytical chemistry by Samuelson (4) appeared. In actuality, this book surveys nearly the whole field of ion exchange. It is of particular value because it makes available in English much of Samuelson's early work dating back to 1939, and

[1] The survey of the literature pertaining to this review was concluded in December, 1953. A few references from early 1954 are included because the reviewer had prepublication copies available in 1953.

[2] The reviewer is indebted to Joan F. Fried for assisting in the compilation of the literature references.

published in his 1944 doctoral thesis (5), particularly on some of the ramifications involved in applying Donnan membrane concepts to ion exchange resins. Two important symposia on ion exchange have been held: one in Germany in October, 1952, under the auspices of the *Deutschen Bunsen-Gesellschaft* and the other in November, 1953, by the New York Academy of Sciences. The lectures given at these symposia were published during 1953 (6, 7).

Several reviews on the applications of ion exchange are available, of which those by Reichenberg (8) and Osborn (9) are especially useful. The latter review consists of a thirty-one page bibliography in two parts; one dealing with specific applications and the other with theoretical considerations. The papers are listed according to subject matter and with the complete titles of each paper. Considering the hundreds of papers published each year dealing directly or indirectly with ion exchange, such an arrangement is a nearly ideal form for an uncritical review. If, in all the chemical literature, only one such review a year appeared, considerable savings of paper and manpower would result.

The annual reports of the Chemical Research Laboratory at Teddington, England, contain a good deal of information on the fundamental and applied aspects of ion exchange (10). Many books contain one or more chapters on ion exchangers, but often these tend to be uncritical and out-of-date to such an extent as to be embarrassing at times to the investigator whose obsolete views are presented. Several chapters in the book on chromatography by Lederer & Lederer (11) are devoted to the theory and application of ion exchange resins. Walton (12) has included a chapter on ion exchange written primarily for the analytical chemist. Emeléus & Anderson (13) in their excellent text present some aspects of ion exchange of interest to the inorganic chemist. The role of ion exchange in the study of complex ions and the relations between chelate formation and separability of inorganic ions by ion exchange is reviewed by Martell & Calvin (14) in their valuable book on chelate chemistry. The book by Mantell (15) on adsorption includes several chapters on ion exchange written primarily for the chemical engineer.

A large part of a long chapter on chromatography by Rauen (16) in the Hoppe-Seyler *Handbuch* series gives, in considerable detail, a well-organized and comprehensive description of techniques and applications of ion exchange with emphasis on biochemical aspects. Considerable information on the interactions of ion exchange resins with proteins, blood cells, and other blood constituents is scattered throughout the book edited by Tullis (17) in which investigations conducted at Harvard in the late E. J. Cohn's laboratories are described. Many of the results are of general interest particularly with regard to the nature of selectivity in ion exchange systems.

New and Modified Resins

Much is being learned about the physical chemistry of ion exchange resins by systematic variations of the polymeric structure. In addition, several

successful attempts have been made to impart specificity to ion exchange reactions by chemical modification of the functional groupings. Specificity in ion exchange resins is induced either permanently, by chemically changing the functional groupings, or temporarily, by absorbing ions on the functional groups which in themselves show high specificity toward a given substance. Many "specific" resins are not necessarily of practical value because they lack chemical and physical stability or else their exchange rates are very slow as compared with ordinary resins.

In his excellent review Boyd (18) devoted several pages to the synthesis and chemical structure of ion exchange polymers. At the present time, fuller details are available in the open literature on the synthesis of practically all commercially available resins. Craig (19) has published a valuable general paper on the synthesis of ion exchange resins which can serve as a good introduction to those unacquainted with the field. A great deal of valuable information on the synthesis and properties of polystyrene and polystyrene-based ion exchange resins is found in the comprehensive monograph on styrene edited by Boundy & Boyer (20). Chapter 14 by G. D. Jones in this monograph, on the chemical alteration of styrene, is superlative.

Feinland, Baldwin & Gregor (21) have prepared sulfonated polystyrene cation exchange resins in which both the degree of cross-linking and exchange capacity can be varied. This was accomplished by the use of 2,5-dichlorostyrene as a copolymer because it was not sulfonated by concentrated sulfuric acid under the conditions employed. The capacity of the resin, therefore, could be controlled by varying the percentage of 2,5-dichlorostyrene in the polymerization mixture. It was necessary to use acetylene tetrachloride as a swelling agent to permit sulfonation to proceed smoothly.

The capacity of carboxylic ion exchangers was varied by Deuel, Hutschneker & Solms (22) while maintaining constant cross-linking. This was done by polymerization of the ethyl ester of acrylic acid with 12 per cent divinylbenzene and *p*-toluenesulfinic acid as catalyst. The resulting ion exchange polymer was stable toward acids and alkali. The ester groups were removed to a desired degree either by treatment of the polymer with concentrated HI at 140°C. or with *p*-toluenesulfonic acid dissolved in acetic acid at 120°C. The swelling of these resins was a function of exchange capacity. In Figure 1 is shown the chemical structure of a partially esterified carboxylic acid resin.

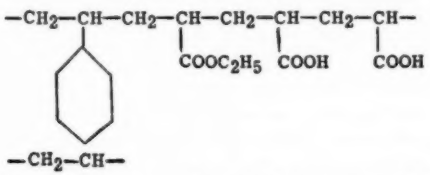


FIG. 1. Partially esterified cation exchange resin prepared initially from the ethyl ester of acrylic acid cross-linked with divinylbenzene with subsequent removal of part of the ester groups (22).

The same group prepared interesting ion exchangers by modification through cross-linking and esterification of naturally occurring polysaccharides such as pectin and polymannuronic acid (22).

Pepper, Paisley & Young (23) have published full experimental details for the preparation of anion exchange resins of varying basicity derived from styrene-divinylbenzene copolymers. These include the types of quaternary ammonium resins available commercially. The observed exchange capacities of these resins agreed with those calculated from the nitrogen contents. In connection with studies of self-diffusion of anions in strong-base anion exchangers (24), a series of resins were prepared in which the anionic size and shape were varied, such as $RNMe_3^+$, $RNMe_2Phenyl^+$, RNPyridinium$^+$, and $RNMe_2PrOH\text{-}2^+$.

Resins containing dibasic phosphonic acid groups and aryl arsonic acid groups have been prepared at Teddington (10). The phosphonic acid resin was prepared by reacting cross-linked polystyrene with phosphorus trichloride under Friedel-Crafts conditions ($AlCl_3$ as catalyst), chlorination of the product, formation of the ethyl ester, and final hydrolysis. The titration data indicated capacities in agreement with the formula [—$CH(C_6H_4PO_3H_2)$—CH_2—] so that the formation of cross-links through phosphinic groups was avoided.

Some aryl arsonic acids combine preferentially with tetravalent metallic ions; several attempts to prepare resins containing this grouping were made. This was accomplished finally by the condensation of dichloro-*p*-arsenobenzoyl chloride with polystyrene. After hydrolysis and treatment with alkaline peroxide a resin containing groups of the type: [—$CH(C_6H_4COC_6H_4\text{-}AsO_3H_2)$—$CH_2$—] were prepared. Other resins containing arsonic groups were prepared by condensation of suitably substituted phenyl-arsonic acids such as 2,4-dihydroxyphenyl arsonic acid with formaldehyde.

Amphoteric resins have been developed as well, at Teddington. The resin containing the grouping: [—$CH(C_6H_4CH_2N[CH_2COOH]_2)$—$CH_2$—] was prepared readily by condensation of imino-diacetonitrile with chloromethylated polystyrene and subsequent hydrolysis of the resulting dinitrile. The titration curve was typical of an amphoteric substance, and the resin was said to have considerable affinity for polyvalent metallic ions.

The preparation of electron exchange resins by Cassidy and co-workers (25) has been continued with the production of improved types. Ezrin & Cassidy (26) have recently published an up-to-date review of their work. Previous preparations of these "redox" resins made from polymerized vinylhydroquinone turned out to be of low molecular weight corresponding mainly to dimers and trimers. After protecting the hydroxyl groups of vinylhydroquinone through the formation of the diacetate or dibenzoate, subsequent polymerization produced high polymers. The protecting groups are removed by saponification with sodium ethoxide in the absence of oxygen. In this manner, preparations have been made of polyvinylhydroquinone, copolymers

of vinylhydroquinone with styrene, α-methylstyrene, 4-vinylpyridine or a copolymer of vinylhydroquinone and styrene cross-linked with divinylbenzene. The esterified polymers gave average molecular weights of at least 40,000 as measured by a static elevation method using a Zimm-Myerson osmometer. The linear hydroquinone polymers are insoluble in organic solvents such as glacial acetic acid and dioxane but readily dissolve when a small percentage of water is added to the mixture of polymer and organic solvent (25, 26). This has been ascribed (26) to a breaking down by the water molecules of cross-links presumably formed by hydrogen bonds between the hydroxyl groups of hydroquinone units in different polymer chains. The free hydroquinone polymers are somewhat unstable to oxidizing conditions but, in general, the redox reactions are reversible (25). In both systems the redox reactions are very slow but by supporting the polymers on filter aids in columns redox reactions could be carried out under flow rates of about 10 ml. per hr. unaided by applied pressure (27).

Manecke (28) prepared a series of high polymer electron exchange resins by the polycondensation of hydroquinone, pyrogallol, and pyrocatechol with formaldehyde and phenol. He systematically varied the molecular ratios of the reactants and found that his best preparation consisted of hydroquinone, phenol, and formaldehyde in a molecular ratio of 1:1:2; however, no further preparative details were given. This redox resin was chemically stable, could be used directly in a column, and could be completely regenerated after oxidation with a ferric sulfate solution in sulfuric acid.

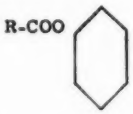
Sansoni (29) has demonstrated that redox properties were associated with ordinary cation and anion exchange resins when the exchanging ions were oxidizing or reducing agents. For example, when a column of a sulfonated polystyrene cation exchange resin was saturated with Fe^{+++} it was capable of oxidizing an alkaline solution of hydroxylamine. Cation and anion exchange resins capable of functioning in systems involving hydroquinone/quinone, methylene blue/leuco-methylene blue, and others were described briefly (29).

While the possibility of preparing ion exchange resins containing optically active groups had been mentioned several times, Bunnett & Marks (30) prepared such a resin. These workers pointed out that a synthetic optically active polymer required a monomer which was (*a*) asymmetric, (*b*) capable of engaging in polymerization, and (*c*) possessed of a functional group which could bind molecules of the racemic substance. One optically active monomer proved to be N-*p*-toluenesulfonyl-L-tyrosine. From it a phenol-formaldehyde type polymer was prepared using phenol as a cross-linking agent; however, the resin was unable to resolve racemic amines. It was believed that the polymer was optically active because of the high specific rotation of a small amount of soluble polymer formed as a by-product and because the monomer was only 17 per cent racemized when it was treated under the polymerization conditions except for the omission of formaldehyde. More recently Grub-

hofer & Schleith (31) apparently produced an optically active resin capable of resolving mandelic acid by reacting optically active quinine with a modified carboxylic resin. Upon treatment of a carboxylic acid resin (Amberlite XE 64) with thionyl chloride and pyridine they obtained a highly reactive product containing about 20 per cent chlorine as indicated by the reaction:

$$R—COOH + SO_2Cl_2 + C_5H_5N \rightarrow R—COCl + C_5H_5NH^+Cl^- + SO_2$$

where R represents the immobile resin "backbone." The preparation reacted with phenol, amino acids, proteins, and many other agents. With phenol, for example, the following product is presumably formed:



In similar vein, the functional groups of an anion exchange resin with primary amino groups ("polyaminostyrene") were modified by Grubhofer & Schleith (31) by diazotization to yield presumably a resin such as $RN_2^+Cl^-$ which reacted with proteins and enzymes. The enzymatic activity was retained.

Modification of the functional grouping of polymeric resins is, of course, analogous to well-known procedures in protein and polysaccharide chemistry, especially in respect to the specificity of serological reactions described in the classical monograph by Landsteiner [(32) particularly Chapter V]. Specific stereoisomerically active antigens, for example, were prepared by coupling an optically active diazotized compound to protein. Many of the methods described by Landsteiner and others have yet to be applied to ion exchange resins for the purposes of imparting numerous types of specificities. Isliker (33) has done outstanding work in this regard by synthesizing antigen-resins. Somewhat in the manner of Grubhofer & Schleith (31) he converted carboxylated resins to the acid chlorides by refluxing the dry resin with thionyl chloride or refluxing the resin for different lengths of time with various dilutions of thionyl chloride in chloroform. Subsequently, it was possible to link soluble and cellular antigens to the resins by a chemical bond. Anion exchange resins were also employed by diazotizing adsorbed dyes which could then be complexed to the antigen.

A promising development is the synthesis of ion exchange resins in the form of the so-called "popcorn" or "cauliflower" polymers [(20), pp. 729–32]. Such polymers have a lower specific activity than the clear polymers. Popcorn ion exchange resins have been prepared by Bodamer (34) by the use of divinylbenzene, butadiene or isoprene as cross-linking agents for methacrylic and acrylic acids. According to Craig (19) these exchangers are much less dense and more porous and can exchange ions more rapidly than conventional ion exchange resins.

Ion-Exchange Equilibria

Donnan (35, 36) has pointed out that:

> . . . the theory of membrane equilibria depends simply on two assumptions:
> a. The existence of equilibrium
> b. The existence of *certain constraints* which restrict the free diffusion of one or more electrically charged or ionized constituents.

The aforementioned assumptions directly apply to ion exchange resins. While the Donnan equilibrium was applied to ion exchange systems many times in the past, the work of Gregor (37) may be said to have stimulated the use of the Gibbs-Donnan formulations by several investigators during the past six years.

From the Gibbs-Donnan relations (35) one obtains equations such as (41):

$$\ln K'' = \frac{\pi}{R}(V^0_{A.R} - V^0_{B.R}) + \ln \frac{\gamma_B}{\gamma_A} - \ln \frac{\gamma_{B.R}}{\gamma_{A.R}} \qquad \text{I}$$

for the cation exchange reaction:

$$A^+.R + B^+ \rightleftarrows A^+ + B^+.R$$

Here K'' is the concentration equilibrium quotient, i.e., an approximation of the equilibrium constant without the introduction of activity coefficients for either phase:

$$K'' = \frac{[A^+]\,[B^+.R]}{[A^+.R]\,[B^+]} \qquad \text{II}$$

The symbols represent the following: [ ], molality; π, the difference in pressure of the two phases; $\overline{V}^0_{A.R}$ and $\overline{V}^0_{B.R}$, the stoichiometric partial molal volumes of A^+ and B^+ in the exchange resin in its standard state taken as infinite dilution; γ, the activity coefficient of the exchanging ion; and R the fixed functional groups in the resin. The presence of a component in the resin phase is indicated by $.R$ as, for example, $A.R$.

Some form of equation I has been introduced by several investigators whose work has been summarized by previous reviewers (1, 2, 18). An intensified continuation of previous efforts has been made during the past year to elucidate the relative quantitative contributions to K'' made by the pressure-volume terms and the activity coefficient terms in equation I.

The resin phase is conveniently treated as a concentrated aqueous solution. The resulting variation of the activity coefficients with cross-linkage in such a system was first brought out by Samuelson (5). The difficulties now associated with attempts to calculate the activity coefficients of the components in the resin phase are paralleled by the unsatisfactory state of knowledge concerning the activity coefficients of solutes in concentrated solutions containing more than one electrolyte. The resin phase may exceed 20 moles of solute per 1000 gm. of bound water. From the historical point of view, it is of interest to recall that as early as 1932 Jenny (38) anticipated this problem:

. . . the exchange reactions on the micelle [ion exchanger] occur in *concentrated* rather than in dilute solutions even if only one single colloidal particle were suspended in a liter of water. Attempts to measure the order of magnitude of ion concentrations on permutit surfaces lead to values >1–2 normal. Under such circumstances the laws of classical chemistry which apply only to dilute solutions cannot be expected to yield good quantitative results. . . .

Consideration of the large changes in activity coefficients of ions which take place in concentrated media leaves little doubt that the activity coefficient factors in ion exchange are always important.

In a qualitative way, and sometimes quantitative way, many of the data in the literature on the variation of K'' can and have been interpreted in terms of known activity coefficient data available in the literature (1). In the exchange of two ions, the activity coefficient changes in the resin phase can be ascribed to several interrelated factors; (*a*) changes in the relative concentrations of the two ions; (*b*) changes in total molality in the resin phase, usually induced by changes in the degree of cross-linkage; and (*c*) decrease in the degree of hydration of the ions partially resulting from factors (*a*) and (*b*).

Extraordinarily small activity coefficients in the resin phase often result from (*a*) ion-pair or chelate formation between the fixed functional groups of the resin and the exchanging ions; (*b*) van der Waals adsorption of the exchanging ions, particularly in the case of large organic molecules, on the resin matrix; and (*c*) formation of an insoluble compound between the functional groups and the exchanging ions.

It is only natural that empirical equations or approaches which have been used to correlate or predict the activity coefficients of ions in concentrated aqueous solutions of mixed electrolytes be applied to the resin phase constituents. Of these, the "Harned rule" (1), first applied to ion exchange systems by Mayer (39) is widely used. Despite the undoubted value of the Harned rule it must be recognized, however, as Harned & Owen (1) point out, that it is an approximation and deviations occur. Actually, it is more likely that improved rules for correlating activity coefficients in these solutions will result from ion exchange studies.

The hydration theories of Stokes & Robinson (40) are being invoked in discussions of exchange equilibria (41, 42). Again, it is hazardous to draw quantitative conclusions concerning ionic behavior in the resin phase on the basis of empirical relations whose success may be due more to coincidence than to fundamental validity. The Stokes-Robinson theory, for example, implies that the parameter a, the mean distance of closest approach in the Debye-Hückel theory, should be an additive function of the ions. For example, the difference between the a'*s* for NaCl and KCl should be the same as the difference between the a'*s* of $NaNO_3$ and KNO_3. The few data in existence show that this principle fails completely as Young points out (43). On the other hand, the Stokes-Robinson concept of "bound" water and "free" water is proving useful in interpretations of the conditions existing in the resin phase.

Despite the surprisingly excellent correlations of ion exchange data afforded by the Harned rule and the Stokes-Robinson hydration theories, it is well to recall that in the past apparently excellent correlation of data were obtained by less sophisticated approaches. Yet, it has turned out that the apparent correlations were due to the insensitivity of the equilibria to the particular type and range of experimental conditions employed. In any event, the problems of ion exchange equilibria are, as Glueckauf (44) has ably pointed out, related to shortcomings of the present theory of electrolytic solutions.

Boyd & Soldano (41) have given careful consideration to the definitions of the terms in equation I. For example, the activity coefficients in the exchanger may be functions of both the composition and swelling pressure, depending on the particular definitions employed in a given formulation. Similar considerations apply to the partial molal volumes terms. Thus, Boyd & Soldano (41) point out further that the relative numerical contribution of the pressure-volume terms and the activity coefficient terms in equation I depends on the concentration scale employed for $\overline{V}^0$. For example, if the values of $\overline{V}^0_{A.R}$ and $\overline{V}^0_{B.R}$ are taken to be as defined in connection with equation I the value of 1.5 ml. mole^{-1} is obtained for H–Na exchange while employment of the partial molal volumes of the hydrated ions gives values varying from about 40 ml. to 62 ml. mole^{-1}. Boyd & Soldano (41) point out that the choice of correct numerical magnitudes involves considerable arbitrariness.

It is well to emphasize that in the selection of equations for use in ion exchange equilibria, one form does not necessarily have a greater fundamental validity than another. It makes no difference, for example, what formula for evaluation of $\overline{V}^0$ is selected provided that the formula is consistent with the number of components which are present and that one formula is used consistently throughout one discussion. Similar considerations pertain to the choice of standard states. The choice of states is largely one of convenience, either experimentally and/or computationally as to what states should be chosen. Thomas (45) in his formulation of the thermodynamics of ion exchange equilibria expresses similar views.

Measurements of the activity coefficients of the diffusible electrolyte in the resin phase have been reported by Davies & Yeoman (46), Gregor (42), using cation exchangers, and Kraus (127), using anion exchangers. The calculation makes use of the Donnan equilibrium and therefore, at equilibrium, it is assumed that the activity of a binary electrolyte in the external solution phase is equal to the activity of the same electrolyte in the resin phase when the resin contains a common ion. Thus, when the hydrogen form of a cation exchange resin or the chloride form of an anion exchange resin is immersed in a solution of HCl we have, in the case of a cation exchanger, disregarding the pressure-volume terms:

$$a_{HCl} = a_{HCl.R} \qquad \text{III}$$

The molal concentrations $[H^+]$, $[Cl^-]$ and $[Cl^-.R]$ are determined by analysis, while $H^+.R$ is evaluated from the expression

$$[H^+.R] = [R^-] + [Cl^-.R] \qquad IV$$

where R^- represents the equivalent concentration of the nondiffusible sulfonate groups, i.e., concentration of charges residing on the resin. Since the activity coefficients of HCl in the outer solution are known, as well as the capacity of the resin and the amounts of water taken up by the resin at different cross-linkages and outer solution compositions, it becomes possible to calculate the activity coefficients of the diffusible electrolyte in the resin phase assuming complete electrolytic dissociation.

The data for several electrolytes showed that the curves for the activity coefficients in the resin phase were of the same shape although lying somewhat below those for the corresponding aqueous solutions. At lower concentration, particularly with the highly cross-linked resin, the values were improbably low. Many workers have observed such anomalies. These have been attributed to fissures or cracks in the resin but such an explanation is at variance with experimental studies where, for example, no uptake of HCl could be observed in 25 per cent cross-linked resin (41a).

When Davies and Yeoman recalculated their data on the assumption that 5 per cent of the water taken up by the resin is in the form of occluded external solution caused by statistical variations in the spacing of cross-links, the data in the dilute solution range (low cross-linked resin) were brought into good agreement. The remaining discrepancies between the experimental points and the curves for pure aqueous solutions were attributed to the mixed electrolyte effect. Calculations were made by means of Harned's rule in the form

$$\log \bar{f}_{\pm} + \alpha[R^-] = \log \bar{f}_{\pm(0)} \qquad V$$

where $\bar{f}_{\pm(0)}$ would be the activity coefficient in the resin phase if all the sulfonate groups were replaced by chloride ions, and α is a constant at a fixed total molality. The values of α were close to those reported for electrolytic mixtures in water and a resulting plot of the values of $\log f_{\pm}$ for HCl and KCl versus ionic strength gave a curve practically coinciding with the data for the resin phase activity coefficients at the same ionic strength.

Gregor (42) reported data similar to those of Davies & Yeoman (46) but dismisses the possibility that the resin, for any reason, occludes significant amounts of external solution because the aggregate volume would have to be 20 to 70 per cent of the volume of the resin. Instead of applying a correction for mixed electrolytes by means of Harned's rule he interprets his data in terms of the double layer concepts of Verwey & Overbeek (47). However, as Gregor indicates, this amounts to saying that the activity coefficient is affected by electrolyte concentrations.

By application of Harned's rule it has been possible, as Davies & Yeoman show (48), to predict the K'' values of K–H and Na–H exchange on a sulfonated polystyrene resin. This work confirms some fairly successful predictions reported earlier by Glueckauf (44) and Duncan (49).

the water in a swollen resin is divided into "free water" and "hydration

Precise measurements of the water absorption by resins of different cross-linkages have been made by Boyd & Soldano (41). From these measurements the swelling pressure, π, was calculated from the equation

$$RT \ln (\bar{a}_w/a_w) = \pi \overline{V}_w \qquad \text{VI}$$

where $\bar{a}_w$ and a_w are the water activities on the cross-linked and uncross-linked resins, while $\bar{V}_w$ is the partial molal volume of water, for which the value 18.06 ml. mole^{-1} was found generally applicable. The swelling pressure, at least in the weakly cross-linked exchangers, turned out to be independent of the salt-form of the resin and to be simply a function of the swollen resin volume. It was further shown that the concentration dependence of the osmotic coefficient for sulfonic acid cation exchangers and quaternary ammonium strong base anion exchangers was analogous to that for 1:1 electrolytes. The equation utilized for the calculation was:

$$\bar{\nu}\Phi = -55.51/\bar{m} \ln (P/P_0) \qquad \text{VII}$$

where $\bar{\nu}$ is the number of ions formed on complete dissociation, Φ is the osmotic coefficient, $\bar{m}$ the molality in the exchanger, P_0 is the saturated water vapor pressure and $\bar{m}$ is determined by measuring the water taken up by an equivalent of resin in equilibrium with a known water vapor pressure, P. By extrapolation of $\bar{\nu}\Phi$ to zero concentration where Φ becomes unity it should be possible to determine $\bar{\nu}$. Unlike strong 1:1 electrolytes $\bar{\nu}$ appears to approach a value of one rather than two, which indicates that the "poly-ions" do not contribute to the thermodynamic properties of the exchanger. To date, the value of $\bar{\nu}\Phi$ has been found to decrease with increasing dilution and a minimum has not yet been observed at the lowest concentrations studied, namely 0.1 M (41). Similar conclusions were reported previously by Glueckauf (44) who, in addition, utilized the osmotic coefficient, Gibbs-Duhem relations, and Harned's rule to calculate the activity coefficients of the exchanging cations in the resin phase. Waxman, Sundheim & Gregor (50) have measured the water absorption of linear polystyrenesulfonic acid and its salt and reported that water adsorption was much less than that found with cross-linked analogues and sulfuric acid. From freezing point measurements the product $\bar{\nu}\Phi$ was found to be dropping rapidly in the dilute regions, reaching a value of about 0.3 in concentrations of 0.1 N; in close agreement with that found for the cross-linked polymers (41, 44). The values of $\bar{\nu}\Phi$ for monomeric electrolytes such as the Na, K, and Li salts of the toluenesulfonic acids are known to approach a value of 2 (41, 44).

Certain anomalies in the water absorption curves of resins with different cross-linkages have been discussed and interpreted in terms of hydration, polymer-polymer interactions, entropy, hysteresis effects, and other factors (41, 50, 51). Considerable progress can be expected in the future from such studies. Of related interest are the important investigations of Pepper & Reichenberg utilizing divinyl cross-linked polystyrene sulfonic acid resins of different cross-linkages (52). By making use of Gregor's theory (37) in which

the water in a swollen resin is divided into "free water" and "hydration water" [a proposal also advanced several years earlier by Jenny (38)] Reichenberg calculated the hydration number of hydrogen ion from three different kinds of experimental data: differences in diffusion rates of Na^+ and H^+ in 5 per cent and 17 per cent cross-linked resins, absorption of nonelectrolytes in the available water in the hydrogen from resins, and swelling in water. All three methods gave approximately five as the hydration number for H^+. See, however, the discussion of the work of Glueckauf & Kitt (53) in the following paragraph. The calculations and methods for determination of hydrated ionic volumes by measurements of swelling are described in detail by Reichenberg (54).

The water content of a 0.5 per cent cross-linked polystyrene sulfonate has been measured by Glueckauf & Kitt (53) at two different temperatures at molar ratios of H_2O to ion as low as 0.5:1. The uptake of water was interpreted as successive addition reactions of the type:

$$H \cdot \bar{R} + H_2O \rightleftarrows [H \cdot H_2O]^+ + H_1$$

$$H \cdot H_2O^+ + H_2O \rightleftarrows [H \cdot 2H_2O]^+ + H_2$$

The results did not, as Gregor (50) also found, follow a Brunauer-Emmett-Teller isotherm previously indicated by the data of Stokes & Robinson (40). An upper number of 4 for the hydration number appeared if it was assumed that association occurred when $-\Delta F = RT$, but if it was stipulated that the free energy should exceed $2RT$ before considering water binding as "moderately firm," then only two water molecules are firmly associated with the H^+ (54). Glueckauf and Kitt conclude "that the concept of a fixed hydration number is too crude and has to be replaced by a quantitative description of the thermodynamic properties of the individual hydration steps."

The exchange reactions of tetraethylammonium ion, Q^+, by a 15 per cent cross-linked polystyrene sulfonic acid cation exchanger have been investigated by Hale, Packham & Pepper (55). Extremely interesting results have been obtained. Thus, when the resin is in the H-form, the uptake of small amounts of Q^+ displaces about 7 molecules of H_2O corresponding to a volume of 210 $Å^3$ for each ion of Q^+ absorbed. From atomic models, the volume of Q^+ was found to be 220 $Å^3$—hence it was concluded that during the initial stages of the exchange the uptake of Q^+ is accompanied by the displacement of a nearly equal volume of water. This result correlates with observations that the amount of Q^+ taken up from neutral solution tends to decrease as the volume of different quaternary ammonium ions increases and that the absorption of a given quaternary ion decreases with increasing cross-linking. When the fraction of Q^+ in the resin is high the resin no longer loses a corresponding amount of water as would be expected from the observation that the uptake of large amounts of Q^+ causes the resin to undergo a partly irreversible distension which corresponds with an apparent decrease of the degree of cross-linking from that of a 15 per cent resin to one of 11 to 12 per

cent. The possibility was advanced that rupture of weak cross-links had occurred (55).

The Gibbs-Duhem equation has been applied for some time in ion exchange systems as a means of evaluating the activity coefficients of the resin phase ions from the equilibrium quotient and known activity coefficients in solution. Davidson & Argersinger (56) have now extended their earlier studies along these lines to include the change in water content of the resin during the exchange reaction. They now regard the pure water-saturated resin as the "standard state" for each resin form. By the additional use of Harned's rule they have been able to improve earlier data for Na–H exchange. Bonner, formerly associated with the Davidson-Argersinger investigators has continued work on Na^+–H^+ and Ag^+–H^+ exchange on Dowex 50 and demonstrated that the equilibrium quotient was related to the maximum water uptake of the resin (57).

McKay (58) has improved the thermodynamic treatment of ternary systems by putting the cross-differentiation relations into a more convenient form. This discussion of the varied applications of his treatment includes an example of its use in ion exchange equilibria. The mole fraction of water in the resin phase is taken into account.

Gregor & Frederick (59) have reviewed in a comprehensive manner the role of the swelling properties of ion exchange resin systems in determining selectivity. Bregman (60) has surveyed additional factors contributing to selectivity, namely resin structure, nature of the acid functional group, mole fraction ratio in the resin, resin capacity, ionic strength of external solutions, and temperature. In the case of K–Li and K–Na exchange studied as a function of the degree of cross-linkage for a polystyrene sulfonic acid resin, Bregman shows that variations in the experimentally determined values of the equilibrium quotient as a function of cross-linkage could be predicted from the known activity coefficients of the corresponding monomeric toluenesulfonates. These results are cited to show that the resin phase activity coefficients predominate over the pressure-volume effects for resins up to 6 per cent cross-linked. Earlier, when Gregor & Bregman (61) had employed the activity coefficients of the chloride salts to predict the variation of K'' with cross-linkage, no such correlation was observed. This led to the conclusion, now reversed, that the experimental variations were due to changes in the swelling pressure rather than the activity coefficient ratios.

An interesting reversal of selectivity is cited by Bregman (60) in which the affinity of the cation exchanger at high cross-linkages is greatest for the ion with the smallest crystal radius. This can be attributed to the dehydration effects which ensue. It should be pointed out that Jenny (38) explained reversals of selectivity in inorganic cation exchange systems as caused by a "reversal of the normal hydration order of the exchanging ions." He also pointed out that "the most hydrated ion will be first affected by dehydration processes." Even earlier, Wiegner and others who studied the exchange of ions in alcoholic solutions of varying concentrations related their results to dehy-

dration effects (62). Also bearing on this subject is the observation that in the anhydrous channels of the ultramarines the selectivity order is: Li > Na > K whereas in the hydrated channels of chabazite the order is K > Na > Li [(63) p. 40].

It is, of course, possible to relate dehydration effects to changes in activity coefficients as required by the Debye-Hückel theory. In any event, careful thermodynamic studies of ion exchange equilibria in alcoholic media should prove very valuable.

The perturbing effect of small amounts of complex-forming structural groups in a supposedly monofunctional cation exchange resin is shown by the work of Fronaeus (64). For Cu^{++}–Na^{+} exchange, for example, he found that even when the concentration of Cu^{++} in the resin was variable but always kept very low in comparison with the exchange capacity of the ion exchanger, the equilibrium quotient varied markedly despite constancy of the ionic strength and pH (=5) of the outer solution. Exchange measurements and pH titrations proved the presence of about 0.25 millimoles per gm. extraneous complex-forming groups, presumably carboxylate. At pH 3.0 the presumed—COOH groups are, as might be expected, blocked by hydrogen ions.

Studies on anion exchange equilibria are not yet as extensive as those on cation exchange equilibria. Isopiestic measurements on the water uptake of the strong base quaternary ammonium anion exchangers by Boyd & Soldano (41) reveal that the osmotic coefficients for the halide-forms of the nominal 0.5 per cent divinylbenzene cross-linked resin at constant molality decrease in the order: $F^{-} > OH^{-} > Cl^{-} > Br^{-} > > ClO_4^{-}$. This sequence, as Boyd and Soldano point out, is the same as that for cesium; thus, it appears that the structurally bound exchange group in the anion exchanger is a large, unhydrated quaternary ammonium cation. It was further concluded that the salts of the anion exchanger, excepting the nitrate and perchlorate forms, are highly dissociated and therefore behave like strong electrolytes. It is possible that the strong interactions by the nitrate and perchlorate ions from the anion exchanger are due to the absence of an appreciable hydration shell, thus permitting a closer approach to the anion exchange groups with a resultant increase in the electrostatic interaction. Differences in hydration may, charge effects aside, account for differences in the observed affinities of anion exchangers for complex ions such as those of many of the chloride and fluoride complexes of transition elements.

Peterson (65) has reviewed the literature on anion exchange processes in general. He has also reported results of studies involving equilibria between aromatic acids and weak base anion exchangers (66). The stronger affinity of aromatic acids for the anion exchanger relative to aliphatic acids was ascribed to "molecular adsorption"—presumably van der Waals attractive forces.

Ion Exchange Kinetics—Batch and Column

Several careful studies have been published in which the effects on the internal diffusion coefficients under varying conditions inside and outside

the resin phase have been reported. It is generally agreed that practically all ion exchange reactions are diffusion controlled. Reichenberg (67) has methodically examined, theoretically and experimentally, the postulates of Boyd, Adamson & Myers (68) that the two principal rate-determining mechanisms are "film-diffusion and particle-diffusion." Reichenberg showed that deductions concerning effects of external solution concentration, particle size, temperature and other factors obeyed equations of the type derived by Boyd, Adamson, and Myers. He also concluded that the diffusion of ions in the resin phase is predominantly governed by the energy of activation for the diffusion of the ions in the aqueous medium existing in the resin (67). To account for the fact that Na^+ diffused 6.6 times as rapidly in a 5 per cent divinylbenzene cross-linked polystyrene sulfonic acid resin as in a 17 per cent divinylbenzene resin he pointed out that the 17 per cent divinylbenzene resin has a smaller volume of diffusion medium (water) per unit volume. Assuming no hydration of the ions, i.e., that all the water in the resin is available as a diffusion medium, then the 5 per cent divinylbenzene resin should exchange 1.46 times as rapidly as in a 17 per cent resin. The observed ratio of 6.6 is obtained, however, if one assumes that the ions are hydrated to the extent of 5 molecules of water per equivalent of resin.

An important series of four papers has been published by Boyd & Soldano (24, 69 to 71) in which, by the extensive use of isotopic tracers, they investigated the self-diffusion of cations in sulfonated polystyrene cation exchange resins (69), the self-diffusion of anions in strong-base anion exchangers (24), self-diffusion of water molecules and mobile anions in cation-exchangers (70), the self-diffusion of cations in hetero-ionic cation exchangers (71). Only a few conclusions from these studies can be mentioned here. However, a concise summary of many of the salient points has been made by Soldano (72). The cationic diffusion coefficient, $\overline{D}$, in the resin phase, was, found to be strongly dependent on the charge, varying from 2.88×10^{-7} cm.^{2} sec.$^{-1}$ for Na^+ to 2.15×10^{-10} cm.^{2} sec.$^{-1}$ for Th^{+4}. Activation energies were temperature but not charge dependent and increased with cross-linking from about 4700 to 10,000 cal. mole^{-1} (69). However, in anion exchange resins, the dependence of $\overline{D}$ of anions on cross-linking and charge was less pronounced. The self-diffusion of Br^- in differently substituted quaternary ammonium type exchangers of constant cross-linkage was more dependent on the size of the fixed anionic functional groups than the charge (24). Using H_2O^{18} as a tracer, it was found that the diffusion of water molecules in and through cation exchangers is not due to transport by mobile hydrated cations since the observed values of $\overline{D}_{H_2O}$ were several times greater than those for cations (70). An interesting method for distinguishing between free and bound water in exchangers was explored by the use of a cation exchanger in the Cr(III) salt form (70). The method was based on the observation of Plane & Taube (73) that the water molecules of $Cr(H_2O)_6^{+++}$ exchange with a measurably slow rate in aqueous solution. It was deduced that not more than 80 per cent of the water in the exchanger can be "free" or solvent water (70). The diffusion of ions in heteroionic cation exchangers showed that, in

to ion exchange processes. A thorough examination of the practical difficul-

general, the diffusion rates of the more mobile cations were lowered, and those of the less mobile ions were increased. Many of the results reported by Boyd & Soldano (24, 69, 70, 71) were interpreted by them with the aid of absolute reaction rate theories (74). Entropy and free energy of activation effects have also been invoked for the explanation of rates of hydrolysis of esters in solutions of water and 70 per cent aqueous acetone by Bernhard & Hammett (75, 76) and by Paulson & Deatherage (77) in studies on the mechanism of protein hydrolysis by ion exchange resin catalysis. The latter group made the interesting observation that blocking or substituting the free amino groups made them resistant to hydrolysis by Dowex 50. They suggested that "a heterogeneous type of catalysis . . . takes place on the surface of the resin particles; blocking . . . the basic groups of the protein interferes with this essential combination."

With many organic ions, the affinity for an ion exchange resin includes additional forces caused by van der Waals attraction. It might be expected that the rates of diffusion in ion exchange reactions would be affected by these attractive forces. Bradley (78) has modified the usual diffusion equations for spherical symmetry to take into account the presence of intermolecular forces. In a hypothetical example involving the rate of diffusion of solute molecules to another solute molecule he finds that the inclusion of a van der Waals force increases the rate of diffusion 28 per cent.

From the historical point of view, it appears desirable to mention the excellent work of Schulze (79) on the rates of diffusion of ions in inorganic cation exchangers. This work, reported in 1914, has been long overlooked. It represents, as far as the reviewer is aware, the earliest work in which the rate behavior in ion exchangers was shown to be diffusion controlled. Schulze applied correctly the equation for solid diffusion and from kinetic data calculated diffusion coefficients which he compared with those obtained from conductivity measurements of the exchanger.

The theory and practice of column and chromatography operations has received considerable attention; especially countercurrent processes. Hiester & Phillips of the Stanford Research Institute (80) have summarized the results and conclusions of exhaustive studies on countercurrent processes contained in eight reports issued by the United States Atomic Energy Commission. In one of these eight reports (81) Hiester and associates have tested on a laboratory scale a countercurrent equilibrium stage operation analogous to well-known multistage mixer-settler units. In their experiments they separated trace amounts of lithium and sodium ions ($\sim$0.03 N) by the use of 1.0 N HCl as elutriant. Zeegers (82) has developed a graphical method of calculating ion exchange processes for continuous systems involving a moving or fixed bed.

In common with Hiester and many workers in the past and present, Zeegers has employed concepts employed in absorption-extraction theories and methods widely used in chemical engineering problems (83) and, in his particular case, has applied the McCabe-Thiele diagram used in distillation (83). Pfeiffer (84) has applied similar graphical methods used in distillation

to ion exchange processes. A thorough examination of the practical difficulties involved in applying continuous countercurrent adsorption processes has been initiated by Swinton & Weiss (85). McCormack & Howard (86) describe a countercurrent ion exchange unit consisting of an endless bed of ion exchange resin enclosed in a porous flexible casing and moved by means of drive pulleys through a series of three tubular liquid reservoirs. The concentrating ability of the unit was demonstrated with copper sulfate solutions in which approximately tenfold increases in the initial concentration were effected using 1–2 *N* sulfuric acid as the regenerating agent.

Gilliland & Baddour (87) and Hagerty & Bliss (88) have developed recovery processes in fixed-bed operations and have obtained correlations from the fact that the rates of ion exchange are controlled by the rate of mass transfer. Gilliland & Baddour (87) were able to correlate many of their data with the Reynolds number.

Contributions to the mathematics of ion exchange and chromatographic processes, particularly under nonequilibrium conditions, have been made, to mention only a few, by Goldstein (89), Bresler (90), Zhukhovitskiĭ *et al.* (91), and Vermuelen (92). The use of automatic computing machines has been applied to ion exchange column calculations by Opler (93) and illustrated with excellent examples. This is a significant contribution since it lends itself to test rapidly various assumptions underlying mathematical theories of column performance, particularly those involving nonequilibrium conditions, and to calculate effects of varying one or more variables at one time.

The problem of the heat developed in an ion exchange column during the elution and regeneration steps has been investigated both theoretically and experimentally for the first time in a thorough and competent manner by Short, Smith & Twigg (94). It was recognized that in small-scale laboratory experiments the heat developed by the reactions proceeding on the resin is generally removed sufficiently rapidly to prevent a substantial temperature rise, but that on the industrial scale where conditions are approximately adiabatic a rise in temperature, at least with certain anion exchange resins, may be serious. Experience shows, they point out, that a "hot spot" corresponding to the reaction front traveled along the bed during elution. Good agreement was obtained between theory and experiment as to the velocity of movement of the "hot spot" and the steady value of the peak temperature.

It is known that in ion exchange processes the presence of an extraneous coating of adsorbed material on the ion exchange resin particles can seriously affect exchange rates. The effect of trace quantities of surface active agents in liquid-liquid extraction processes was shown by Garner & Hale (94a) to have marked effects on the rates of mass transfer. Their paper, in which the problem is also reviewed, has obvious bearing on the ion exchange field.

Nonaqueous Systems

Evidence that a cation exchange resin (Dowex 50) can undergo cation exchange in liquid ammonia has been claimed by Keenan & McDowell (95) who, through a column of the ammonium form of the resin, rendered anhy-

drous, passed "a solution of liquid ammonia which contained the products of the reaction of potassium with monoammino boron trifluoride." The resin quantitatively removed potassium but elution with 1.5 M NH_4Cl solution failed to remove more than a few per cent of the retained potassium. Unless equivalent exchange, reversibility and other experiments are carried out, it is not possible to make deductions as to the mechanism of their reaction. In earlier work, Bergin & Heyn (96) used a cation exchange resin membrane as an electrode in liquid ammonia. From the following cell system:

	Liquid Ammonia			Alcohol		
Ag	$AgNO_3$ 0.001 M	NH_4NO_3 (varying concentrations)	Membrane	NH_4NO_3 0.001 M	$AgNO_3$ 0.001 M	Ag

they were able to determine the ratios of activity coefficients of ammonium nitrate in liquid ammonia. The results were said to agree closely with those obtained by earlier investigators using a different electro-chemical method.

A wide range of experiments in the behavior of several types of ion exchange resins in different solvents were made by Bodamer & Kunin (97). Air-dried resins for practical reasons were employed and their properties, swelling and exchange capacity, were determined in several different solvents including ethanol, acetone, glycerol, pyridine, acetic acid, benzene, and dioxane. In most cases, true ion exchange reactions occurred just as in water. Polar solvents caused greater swelling and in polar solvents exchange occurred most rapidly.

The effect of varying concentrations of methanol and ethanol in water on the equilibrium quotient, K'', for cation exchange reactions involving alkali metals and alkaline earth cations was carefully determined by Sakaki & Kakihana (98). Linear relations were found between log K'' and the reciprocal of the macroscopic dielectric constant, D, as long as $D > 55$.

In an interesting and suggestive study, Katzin & Gebert (99) investigated the uptake of HCl, LiCl, and the chlorides and nitrates of divalent transition elements by an air-dried strong base anion exchange resin from their acetone solutions. The uptake of the solutes was not through ion exchange but was characterized by the molecule as a whole disappearing from the liquid phase. In the case of cobaltous chloride, the uptake increased as the equilibrium H_2O content of the resin increased. However, the uptake of cobaltous nitrate was independent of the water content of the resin. Pyridine had an inhibiting effect on the absorption of cobaltous salts. One mechanism for the uptake of the transition metal salts in acetone may be, according to Katzin and Gebert, as follows:

$$R^+X^- + MX_2 = R^+(MX_3)^-$$

in which R^+ represents the resin cation.

It is well known that the rates of diffusion of ions decrease in organic solvents or in mixtures of organic solvents and water as compared to water

itself. Consequently, it would be expected, as is generally found, that ion exchange reactions would be slower in nonaqueous solvents. Important column studies in nonaqueous solvents now published by Vermeulen & Huffman (100) and Chance, Boyd & Garber (101) were mentioned in last year's review (2). It is worthwhile noting in addition that the former investigated the uptake of various amines in several different absolute alcohols and benzene by the hydrogen form of Dowex 50. The effects of H_2O in the resin and solvent were also studied. Rates of exchange in water were 1000 to 2500 times as rapid as in the organic solvents. Effects of diffusion, degree of reversibility of exchange, and viscosity were among the various factors which were evaluated quantitatively.

Electrochemistry of Ion Exchange Resins

Research activity on the electrochemical behavior of ion exchange resins and membranes might be described as intense. In view of the comprehensive treatment of the subject by the previous reviewers (2, 3) we will treat the electrochemical aspects briefly. Fortunately, a comprehensive and elegant review has been recently published by Spiegler (102). Important additional reviews have been put out by Winger, Bodamer & Kunin (103), Sollner (104) and several articles in the March, 1953 issue of the *Zeitschrift für Elektrochemie* (6).

Scatchard (105) has presented in rigorous fashion the equations for the electromotive force of ion exchanger electrodes developed from the general equation for the electromotive force of a cell with transference. His treatment is particularly important because he includes the effect of water transfer—one of the largest factors causing deviation from ideal electrode behavior. Marinsky & Katz (106) used H_2O and D_2O in an attempt to determine the degree of separation of H and D resulting from endosmotic water transfer across a cation-exchange resin membrane. While the ratio of H_2O to D_2O transferred was greater than the ratio in the solution from which transfer occurred, the separation factor did not exceed 1.07 ± 0.02; much less than the calculated values.

Anion activities of Cl^- and SO_4^{--} in solutions have been measured by Sinha (107) with anion exchange membranes. Membranes were prepared by molding a mixture of finely powdered resin and polystyrene under pressure (4000 lb. per sq. in.) and elevated temperature (120 to 130°C.). The electrodes behaved in ideal fashion in dilute solutions (<0.1 *M* for Cl^- and 0.01 *M* for SO_4^{--}).

Honda & Bizen (108) point out that an observed change in resistance of a bed of a cation exchange resin in water or very dilute acid (10^{-5} *M* HCl) might be used as a sensitive test for determining the solubility of resins. Miyamoto & Sasaki (109) formed a film of oxidized hydroquinone-formaldehyde resin on a flat surface of Pt. They found a linear relation between the potential measured by the Pt electrode in the range pH 0.5–8.

Spiegler & Coryell (110) demonstrated that the mechanisms of diffusion

and electrical conductance in the resin are similar. The self-diffusion coefficients of Na^+, Zn^{++}, and Cd^{++} ions were determined from the observed spread of radio-tracers on cation exchange membranes. The observed values of $\bar{D}$ were in reasonably good agreement with those measured by electrical conductance of the membranes by means of the Nernst-Einstein equation:

$$\bar{D} = RTm/ZF = 2.66 \times 10^{-7}\Lambda/Z \text{ at } 25°\text{C.} \qquad \text{VIII}$$

where R is the gas constant (watt deg.$^{-1}$ mole^{-1}), T the absolute temperature, F Faraday's constant (coul. eq.$^{-1}$), Z the valence of the ion, m its electrical mobility (cm.^{2} volt^{-1} sec.$^{-1}$) and Λ the equivalent conductance of the resin (mho cm.^{2} eq.$^{-1}$). The same equation was employed in 1914 by Schulze (79) in his work on inorganic cation exchangers mentioned earlier in this review. Spiegler suggests that the conductivity of membranes may be used to determine the degree of cross-linking.

Separations—Purifications—Preparations

Several separation techniques, well-known in chromatography, are being applied with excellent results in systems involving ion exchange resins. For example, Vickery (111) obtained a striking improvement in the degree of separation of Nd and Pr ions by elution from a cation exchanger with ethylenediaminetetracetic acid (EDTA) when Mn ions were deliberately added. The Mn elution curve was interpolated between those of Nd and Pr. A similar technique was employed in 1937 by Schwab & Jockers (112) for the separation of cations on alumina by interposing a third cation between a pair being separated and more recently by Tiselius & Hagdahl (113) who call the technique "carrier displacement."

The technique of precipitation chromatography has often been employed in the past, though in some cases unwittingly and with undesirable results. An anion exchanger, for example, can be converted with a given anion which forms selectively an insoluble compound with one or more desired substances. Anion exchange resins saturated with H_2S have been employed several years ago by Gaddis (114) as a precipitant for cations in qualitative analysis and by investigators on the Plutonium Project. Precipitation chromatography was employed recently by Komlev & Tsimbalista (115) in qualitative semimicroanalysis, but the resin served merely as a filter, retaining precipitates by "mechanical entrapment." An efficient application of precipitation chromatography was made by McIsaac & Voigt (116) who prepared P^{32} resulting from the nuclear reaction $S^{32}(n, p)P^{32}$. A cation resin was converted to the ferric form and subsequently 2 M NH_4OH was passed through the column. The iron was converted to the hydroxide. The resulting exchange bed was highly selective for phosphate while sulfate was unadsorbed. Dilute NaOH served to elute the phosphate in carrier-free form. Maier (117) cites a case in which a weak base anion exchanger was used successfully (or so it was thought at first) for the removal of fluorides. Later studies showed that its capacity was derived from precipitated aluminum oxide formed in the column during regeneration with alum.

"Gradient elution" chromatography was recently introduced by Alm & Williams working in Tiselius' laboratories (118), by Marshall, Donaldson & Friedberg (119) and by Busch, Hurlbert & Potter (120). In this type of elution the concentration of eluant is gradually increased and has the effect of reducing tailing in nonlinear adsorption isotherms. Step-wise elution as often practiced in ion exchange separations works best with linear adsorption isotherms. Gradient elution was applied in ion exchange chromatography by Busch, Hurlbert & Potter (120) who separated organic acids from anion exchange resins by continuously increasing the concentration of the eluting acid. Improvements in technique as well as in the formulation of suitable equations have been proposed by Cherkin, Martinez & Dunn (121) and Laksmanan & Lieberman (122).

Another variation in separation technique has been applied by Spedding, Powell & Wheelwright (123, 124) for improving rare earth separations. The rare earths are eluted with EDTA solutions (buffered with ammonium hydroxide) through a resin bed saturated with Cu^{++} as the "retaining ion." The Cu^{++} is complexed by the EDTA more strongly than many of the rare earths so that the Cu^{++} is eluted as an EDTA complex while the rare earth complexes are decomposed; hence the rare earth cations are retained by the cation exchange resin (124). The method allows 10 to 20 times as much rare earths to be used as with the usual citrate solutions and the separation factors are better. Previous work (123) using Fe^{+++} as the retaining ion was unsatisfactory because insoluble $Fe(OH)_3$ would form at high pH.

Mayer & Freiling (125) have also found that EDTA was the best eluting agent for tracer amounts of rare earths from the standpoint of selectivity but in the low pH range which they employed (pH = 3.62) the low solubility of EDTA was a handicap. Lactic acid was found by them to be markedly superior to the usual citrate solution for elution of tracer amounts of rare earths, at least for the separation of Y, Tb, Eu, and Sm.

Another interesting development was the demonstration by Kraus, Nelson & Baxter (126) that acids can be separated from metal salts by anion exchange. They point out that a strong base anion exchange resin in the sulfate or other polyvalent anion form functions as a base which can take up acids according to a reaction such as:

$$\overline{SO_4}^{--} + HX \rightleftarrows \overline{HSO_4}^{-} + \overline{X}^{-}$$

and

$$\overline{SO_4}^{--} + H_3O^{+} + HSO_4^{-} \rightleftarrows 2(\overline{HSO_4}^{-}) + H_2O$$

The separation of sulfuric acid from copper sulfate solution was demonstrated. Kraus and associates (127 to 130) have continued their anion exchange studies in concentrated HCl solutions and demonstrated excellent separations of transition elements, in particular. In a comprehensive study of the uptake of metal salts in HCl solutions (130) a reasonable parallel was drawn between absorbability in anion exchange and extractibility into ethers from HCl solutions since, in both cases, the formation of chloride complexes is necessary. On the other hand, while anion exchange absorption may al-

ways occur for elements which show good ether extraction, it is possible, the authors point out, that anion exchange absorption may occur without concordant ether extraction.

The uptake and elution of numerous metals by a strong base anion exchange resin was investigated by Hicks *et al.* (131), especially with reference to radiochemical separations and preparation of carrier-free tracers. Brooksbank & Leddicotte (132) have demonstrated how ion exchange techniques coupled with neutron activation are used to analyze for trace elements in biological materials, metals, ores, etc. Tobias *et al.* (133) have also employed ion exchange for the determination of traces of inorganic elements in tissues and blood cells following neutron activation. Ashed tissue was absorbed on a cation exchanger and eluted with HCl.

It is possible to mention only a few of the many papers dealing with the use of ion exchange in radiochemistry. A valuable paper by Rupp & Binford (134) describes in detail the production of radioisotopes at Oak Ridge and describes for each radioisotope the principle purification method employed. About 20 per cent of all the nuclides produced at Oak Ridge involve ion exchange operations. Kayas (135) has employed ion exchange extensively in radiochemical studies, especially in studies of Szilard-Chalmers reactions, as for example, the separation of Br^{80} from irradiated $C_2H_4Br_2$. The separation of technetium following neutron irradiation of a molybdenum target was described by Hall & Johns (136).

A large number of papers are now appearing dealing with the separation of fission products, neptunium, thorium, and other elements from solutions of uranyl salts. Thus, Johansson (137) separated Np and Th from fission products directly from irradiated uranium. In one case the uranyl ion was preferentially desorbed from the cation exchanger with 2 *M* HCl whereupon the Np^{239} and Th^{234} were eluted in separate bands with 0.5 *M* HF. Variations in separation efficiency were obtained by changing the valence state of Np through redox reactions. By means of ion exchange Isaac & Picciotto (138) were able to measure directly the ionium (Th^{230}) content in samples of deep sea sediments. Uranium-X (Th^{234}) was added directly to a solution of a sample as a tracer for ionium. Subsequently, the solution, 0.5 *N* in HCl, was passed through a cation exchange resin. Elution with 2 *N* HCl removed most of the cations including uranium and radium. This was followed by elution with 0.5 *M* oxalic acid which eluted thorium and polonium isotopes. Radiochemical assay of the α-radiation from the ionium completed the analysis. Aldrich, Doak & Davis (139) have made excellent use of ion exchangers for separating cations from rocks for age determinations. Dolar & Draganić (140) separated rare earths from uranium by absorbing UO_2^{++} and the rare earths on a cation exchanger, eluting UO_2^{++} with 1 *N* oxalic acid, and finally eluting Ce, Eu, and Y with 5 *N* HCl. Dizdar (141) analyzed for traces of cadmium in uranium by selective elution of the absorbed UO_2^{++} ions with 0.5 *N* oxalic acid and elution of Cd^{++} with 1 *N* HCl. The Cd^{++} was then assayed polarographically and spectrographically.

Separation of rhodium from uranium fission products and the four plat-

inum group metals, Pd, Rh, Ir, and Pt, from one another was accomplished by stepwise elution with HCl from a cation exchanger by Stevenson *et al.* (142). The Pt passes through unabsorbed from a solution of perchloric acid while Pd, Rh, and Ir are removed by elution with 0.05–0.5 *M* HCl, 2*M* HCl, and 4–6 *M* HCl, respectively. MacNevin & Crummett (143) separated the platinum group metals by utilizing the fact that they form complex halide anions. Consequently, they utilized anion exchange resins to absorb the complexes. On the other hand, the complex ammines of the Pt group behave as cations and can be separated by means of cation exchange resins.

Freund & Miner (144) determined Al in Zr by absorbing the fluoride complex of Zr on an anion exchange resin while the Al passed through unabsorbed. Separation of Sb^{125} from tin was accomplished by Kimura *et al.* (145) by selective elution of Sb^{125} with 0.4 per cent tartaric acid in HCl at pH 1. Minami & Ishimori (146) made a Ba–Pb separation by selective elution from a cation exchanger of Pb^{++} with ammonium acetate solution at pH 6.1 while the Ba^{++} was eluted with 10 per cent NH_4Cl. Aoki (147) separated selenium and tellurium by selective elution with HCl solution. Buchwald & Wood (148) removed copper from mineral oil in an interesting manner. They removed the water from the hydrogen form of a strong acid cation exchange resin with 2-propanol. The resin then removed copper quantitatively from mineral oil. Excess oil was removed with 2-propanol and the Cu eluted with 10 per cent sulfuric acid.

Only a few of the many interesting ion exchange operations involving organic and biochemical substances can be mentioned. Hutchins & Christian (149) separated, for purposes of qualitative and quantitative analysis, several different S^{35}-labeled sulfonamides by chromatographic elution from a cation exchanger with HCl solutions. By the use of cation exchange resins a simple microanalysis of organic salts was developed by Van Etten & Wiele (150). The method utilized either the inorganic salt or an organic acid or salts of organic bases. Upon passage through the hydrogen form of the exchanger, the displaced H^+ was titrated. In similar fashion it was possible to determine sodium chloride in dextran solutions. An excellent monograph by Sjöström (151) has been issued on ion exchange for the separation of ketones of different structure using bisulfite as the complexing agent. The procedure is derived from the work of Samuelson [(4) p. 190]. A highly effective separation of nearly all the nitrogenous compounds in bacterial hydrolyzates by the use of a single column of a cation exchanger using HCl as an elutriant was accomplished by Wall (152).

Cohn (153) has presented an authoritative review of the separation of biochemically important substances by ion exchange chromatography. Ion exchange has always been useful in preparing different salt forms of clays, dyes, etc., since the exchangeable ions undergo exchange whether or not the oppositely charged ion is a polymer, or insoluble. Alexander (154), for example, prepared pure monosilicic acid by treatment of a pulverized, hydrated, crystalline sodium metasilicate with an aqueous slurry of a cation exchange resin in the hydrogen form at 0°C. Baker, Gallagher & McCutcheon (155)

converted ammonium dodecamolybdocerate IV octahydrate to the free heteropoly acid. Only the ammonium ion was removed by the exchanger; no cerium or molybdenum could be detected in the used regenerant. McCutcheon & Schuele (156) prepared solutions of the free acids of complex anions of cobalt and chromium by a similar procedure. Lewis (157) determined the degree of conversion of bentonite suspensions when percolated through cation exchange resins. The rate of conversion to the hydrogen form was the most rapid.

The techniques of ion exclusion are being extended by Wheaton & Bauman (158). In an excellent paper which cites new work and reviews the principles of the method, separations are reported of ionic from nonionic components. A new series of separations of this type was reported, based on earlier work in which it was shown that nonionic substances differed considerably among themselves in the extent of exclusion. The distribution coefficients for numerous organic molecules were determined for systems involving cation and anion exchange resins. From these coefficients it was possible to predict by means of the plate theory the degree of separation obtainable in a column run. Efficient separations were demonstrated upon mixtures which included formaldehyde–acetone, glucose–acetone, glucose–methanol, and in a multi-component system the substances sucrose–glycerine–triethylene glycol–phenol.

In concluding this section it is well to point out one outstanding aspect of ion exchange operations. This is the fact that the single reagent, hydrochloric acid, in varying concentrations depending on conditions, can be used to resolve mixtures of practically every known element or compound, organic or inorganic, into their components. This includes such separations as rare earths from transuranic elements, nucleic acids, amino acids, alkali metals from one another, organic acids, and many others too numerous to mention here. The effectiveness of HCl is due to several factors, among which are: (*a*) its cationic displacing ability can be adjusted by simply changing the concentration; (*b*) it generally forms soluble salts; (*c*) at high concentrations it forms chloride complexes of varying stability and charge; (*d*) it is a strong acid and can be used to vary the degree of ionization of acidic and basic substances. Naturally, inherent differences in substances themselves which are being separated, such as electronic configuration, size and radius, and degree of dissociation are concomitant factors in the remarkable versatility of HCl. Additional factors such as its chemical stability, formation of a constant boiling mixture, weak oxidizing and reducing qualities, solubility in many organic solvents, and volatility are also important considerations. While many other acids (such as HBr, HF, oxalic, and sulfuric acids) have special and sometimes unique uses and possess many of the qualities of hydrochloric acid, it is unique in possessing a larger number, over-all, of generally desirable qualities as an agent in ion exchange separation.

Ion Exchange as a Tool in the Study of Electrolytic Solutions

Ion exchangers have and are being used for quantitative and qualitative

investigations of the properties of substances in solutions to an extent that is far greater than is commonly realized. Only the briefest outline of investigations in this field can be given here. The discussion to follow is, in view of space limitations, mainly historical. Brief reviews by Samuelson [(4) pp. 244–58] and Schubert (205) are available.

As far as can be ascertained, Günther-Schulze (159, 160) in 1922 was the first to recognize and utilize synthetic ion exchangers as a tool for studies of electrolytic solutions. He assumed that the decrease in Cl^- concentration in concentrated solutions which occurred when the chloride salts of Cu^{++}, Ba^{++}, $Zn,^{++}$ Cd^{++}, and other divalent cations were equilibrated with inorganic cation exchangers was due to the formation of cationic complexes such as $CuCl^+$ which were taken up. In principle, Günther-Schulze's ingenious approach was correct, though the results obtained were questionable because of the instability of the exchanger, neglect of water absorption by the exchanger, and other factors. Actually, using organic cation exchange resins, Samuelson (161) reinvestigated systems similar to those studied by Günther Schulze and found no evidence for complex formation after making appropriate corrections for Donnan and other effects. On the other hand, while the alkaline earths were found by Kraus (130) in his anion exchange studies, not to form chloride complex ions even in 12 *M* HCl, he did demonstrate that negatively charged chloride complexes of Cu^{++}, Co^{++}, Zn^{++}, Fe^{++}, and Mn^{++} were formed in HCl solutions, beginning, in some cases, in HCl solution less than 2 *M* (128).

Shortly after Günther-Schulze's work, Gustavson (162, 163) began investigations on the nature of chromium complexes, especially in relation to the tanning process, using at first the inorganic zeolites and later the organic exchangers. In his early work, Gustavson determined the degree of uptake of chromium following percolation through columns. In this way he was able to differentiate among cationic, anionic, and neutral complexes containing chromium. Later work involved equilibrium measurements as well. Gustavson has continued his important studies to the present day and has included variables such as effect of cross-linkage, functional groupings in the resin, anion exchangers, etc. For an adequate summary and list of references of his work the reader is referred to some of Gustavson's more recent articles (164 to 168). Interesting studies similar to Gustavson's include those by Adams (169), Serfass *et al.* (170), and Theis & Thorstensen (171).

In 1944, Samuelson (172), using the synthetic organic exchange resins, investigated the composition of the ferric metaphosphate using the column technique essentially as applied by Gustavson (162). In 1946, he extended the equilibrium technique of Günther-Schulze and, by means of equations based on the Donnan equilibria, he determined the dissociation of ferric polymetaphosphate solutions (173). In principle, the method consisted of the determination of the activity of a cation in the presence and absence of varying concentrations of the complexing agent, keeping other factors as constant as possible.

It is apparent that the use of ion exchange as a physico-chemical tool was

stimulated initially by the desire to elucidate the structure and composition of complex ions. However, in 1932 it occurred to Vanselow (174) that ion exchange reactions could be utilized for the determination of activity coefficients in mixed electrolytes. This important proposal by Vanselow had considerable merit, though, at the time it was put forth, he assumed that the activity of each ion in the exchanger phase was equal to its mole fraction. By the use of tracers, however, it is now possible to extend the method so that it can yield absolute values of the activity coefficients as will be pointed out shortly. In 1945, Flagg & Bleidner (234) used acid- and base-regenerated alumina to determine whether element 43 was in a cationic or anionic state.

The general usefulness of ion exchange as a physical-chemical tool, particularly in conjunction with radioisotopes, was pointed out by Schubert (175). This publication was taken from investigations begun on the Plutonium Project in 1944 and reported early in 1945 (176, 177). In a paper published in the open literature (175) it was pointed out that ion exchangers can be used for: (*a*) the determination of the dissociation constants of complex ions; (*b*) the rapid detection and evaluation of the relative complex-forming properties of organic salts; (*c*) measurements of the activity coefficients of tracer substances in the presence of large concentrations of foreign electrolytes; (*d*) the detection and study of radiocolloids; (*e*) the qualitative determination of the charge of a substance in solution; and (*f*) the determination of the valence and relative basicity. Shortly thereafter, much of the material which appeared in references (176) and (177) was published in the open literature (178 to 181). The measurements on complex ion stability were particularly reassuring inasmuch as the values (178) for formation quotients for complexes of alkaline earths and the deduced composition of the complex agreed with those reported in the literature. This was the first demonstration of the reliability of the ion exchange method for complex ion studies, on the basis of independent unambiguous evidence. Since the technique involved carrier-free radiotracers it was possible to determine the composition and stability of complex ions under such conditions that the composition of the resin and solution phases remained constant and no correction for the amount of the organic ligand bound by the metal ion need be made. Other important advantages were that the method permitted the measurement of complex formation by several different metals in the same solutions and under varying conditions of temperature, ionic strength, and solvent changes (182, 183).

The use of carrier-free tracers for measurement of absolute or relative coefficient measurements in mixed electrolytes is particularly valuable. For example, by working in a region where pressure-volume effects are negligible one can apply the simple Donnan equations to determine the activity coefficient ratio of the exchanging ions in the resin phase provided that the outside solution is sufficiently dilute so that the activity coefficients of the salts in the external solution are known exactly. For example, consider a 10 per cent cross-linked cation exchanger wholly in the K^+ form immersed in a solution sufficiently dilute in KCl so that the Debye-Huckel limiting law holds, and containing carrier-free amounts of Na^+. In such a system one can

calculate from the Donnan equilibrium the activity coefficient ratio of $\overline{Na}^+/K^+$ since that of K^+ and Na^+ is known. Then the concentration of KCl in the external solution can be varied over a wide range. Since the activity coefficients of KCl are known exactly, the only unknown is the activity coefficient of the NaCl, assuming, as is often the case, that pressure-volume effects can be disregarded. The absolute activity coefficients of carrier-free $Ba(NO_3)_2$ in uranyl nitrate solutions was measured by Schubert (180) but in this case the activity coefficients in the resin phase were disregarded. Fortunately, however, recalculation of the data in the manner described in this paragraph gives results in agreement with the published ones. Betts & MacKenzie (184), in a comprehensive study, employed in principle the method described by Schubert (175, 180) and were able to measure the activity coefficients of the chlorides of sodium, potassium, rubidium, and cesium at effectively zero concentration in hydrochloric acid solutions from 0.005 to 1.5 *M* and of sodium chloride in solutions of lithium and potassium chlorides.

The reports published by Schubert (176, 177) on the Plutonium Project, particularly those involving the measurement of complex ions and activity coefficients were successfully utilized with suitable and important modifications by several workers on the Plutonium Project, particularly by Mayer and associates who studied the complexes of rare earths with citrate (185), and the activity coefficients and association constants of cerous salts with inorganic anions (186, 187, 188).

The differences in uptake between colloids and ions by ion exchangers can be exploited as a means of studying the properties of colloids, particularly of radiocolloids, in different environments and as a means of effecting separation of elements by complex ion formation. For example, studies on the ion exchange behavior of zirconium and niobium showed that they were not taken up as ions but as colloids (179, 181). The addition of complex-forming agents such as fluoride and oxalate however caused these elements to behave as true ions and to be absorbed by a cation exchanger depending on the concentrations of the complexing agent. This behavior was correctly ascribed to the formation of complex anions. As a matter of fact, it appears possible to effect far better separations of these elements as complex ions by means of cation exchangers than by anion exchangers. This can be done particularly under conditions where the concentration of the complexing agent is sufficient to prevent precipitation of the ions and yet be small enough to permit uptake of one of the dissociated ions by the ion exchanger. For example (179), the distribution coefficient of Nb^{95} in 0.5 *M* fluosilicic acid for a cation exchange resin averages 14 while under identical conditions that of Zr^{95} is 0, giving a separation factor which approaches infinity!

The number of publications dealing with the use of ion exchange as a physico-chemical tool has been increasing steadily during the past few years. Of particular interest is the work of Fronaeus (189 to 194) who developed the ion exchange method for complex ion measurements so as to render it possible to calculate the successive complexity constants of complexes. Using cation and anion exchangers he has reported results for systems involving

copper, nickel and cerous acetate, cerous sulfate, nickel thiocyanate, and cadmium iodide and bromide.

Other interesting work that has been published deals with topics such as isomer detection, isoelectric points of proteins, degree of polymerization, support of the electronic configuration of the actinide elements, and many others. For convenience and as a guide, most of the different kinds of applications that have been made in which ion exchangers have been used as a tool are summarized in Table I.

TABLE I

LITERATURE DEALING WITH THE USE OF ION EXCHANGERS AS A TOOL FOR THE STUDY OF ELECTROLYTES

Subject	References
Composition and Stability of Complex Ions	
Copper salts (using inorganic exchange)	159
Halides of divalent cations (using inorganic exchangers)	159, 160
Chromium Complexes	4, 162 to 171, 224, 233
Halides of transition elements	128, 130, 161, 236
Hafnium, zirconium, niobium, tantalum, and protactinium halides	179, 226, 236
Alkaline earths including radium with organic acids	178, 182, 183, 227
Effects of temperature, ionic strength and solvent	182
Complexes between calcium phosphates and phytate	231
Transuranic chlorides and citrates	195 to 198
Cadmium halides	192
Dissociation of polyphosphates (ion exchange membranes)	217
Beryllium citrate	229
Rare earth citrates	185
Calcium bicarbonate	232
Calcium complexes with adenosine di- and triphosphate	230
Cerous salts	186, 187, 188, 191, 192, 193
Ferric sulfate	228
Copper and nickel acetates	189, 190
Nickel thiocyanate	194
Silver and copper complexes with ammonia and amines	235
Calcium-protein binding	214, 215, 216
Pyridine-iodide complexes	223
Iron phosphates	225

TABLE I—(*continued*)

Subject	References
Activities and Activity Coefficients in Mixed Electrolytes	
Barium-cadmium chlorides	174
Barium nitrate in uranyl nitrate	175, 180
Chlorides of alkali metals in hydrochloric acid	184
Sodium chloride in lithium and potassium chlorides	184
Cerous salts	188
Activities of ions with ion exchange electrodes	213, 216
State of Element in Solution	
Exchange reactions between ferro- and ferricyanide	218
Hydrated ionic volumes	204
Radiophosphorus by sectioned ion exchange column	208
Zirconium ions	179, 209, 210
Bond types in cobalt complexes	219
Charge and Valence	175, 206
From swelling characteristics	202, 203
Charge of protactinyl ion	207
Zirconium ions	209, 210
Charge on dyes	222
Element 43	234
Ytterbium oxalate	237
Polymerization and Colloid Formation	
Zirconium ions	179, 209, 210
Beryllium salts	211
Radiocolloids	176, 179, 181
Aging of colloidal solutions	220, 221
Discovery of New Elements, Compounds, and Isomers	
Transuranics	195 to 198
Element 61	199
Isomeric nucleic acids	153, 200
Orotic acid	201
Electronic Configuration in Transuranic Elements	195 to 198
Isoelectric Point of Proteins (Gelatin)	212
Volume Changes of Resin as Physico-Chemical Tool	202, 203, 204

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STATISTICAL MECHANICS OF TRANSPORT AND NONEQUILIBRIUM PROCESSES[1,2]

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Introduction

The aim of statistical mechanics is to develop a formalism from which one can deduce the macroscopic behavior of physical systems composed of a large number of molecules from a specification of the component molecular species, the laws of force which govern intermolecular interactions, and the nature of their surroundings.

In the field of nonequilibrium statistical mechanics one attempts to derive phenomenological equations such as the equations of hydrodynamics and to compute the parameters of such equations (diffusion constant, viscosity coefficient, etc.) from molecular models. One tries to predict chemical reaction rates, understand the mechanism of irreversible processes such as the decay of turbulence, and estimate relaxation times for various kinds of degrees of freedom to come to equilibrium with each other.

One of the striking properties of systems of large numbers of particles is the irreversibility of their behavior and the rapidity with which their past history is erased as they approach equilibrium. The equations which describe irreversible processes such as heat conduction and diffusion are generally first order in time while the equations of motion of particles and waves are second order in time.

Since the second order equations are invariant with respect to time reversal, their solutions form a basis for describing the manner in which a system must have achieved a given state as well as for predicting its future behavior. Although the Maxwell and Schroedinger equations are first order in time, their solutions are reversible for special reasons.

The central problem of nonequilibrium statistical mechanics is to derive a set of equations which describe irreversible processes from the reversible equations of motion. At first glance this aim seems paradoxical in view of the "Wiederkehrsatz" of Poincaré which asserts that almost every state of a closed, isolated dynamical system will eventually be nearly reachieved (the

[1] The survey of the literature pertaining to this review was completed in January, 1954.

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words "almost every" and "nearly" have a precise mathematical meaning.) It is felt, however, that the periods of Poincaré cycles increase with the number of the degrees of freedom, eventually approaching infinity, and that absolute irreversibility is a limit phenomenon. The time scale associated with a system of 10^{23} particles can be expected to be so long that its behavior mimics that of an infinite system extremely well. The discussion of irreversibility in classical systems in the famous encyclopedia article of P. & T. Ehrenfest (1) has never been significantly improved upon. An important analysis of the ergodic hypothesis in equilibrium statistical mechanics has been made by Khinchine (2).

The Ehrenfests (3) studied a nonmechanical model (which has Poincaré cycles) for the exchange of heat between two systems. It involves the random drawing of balls from either of two urns, with the number of balls in each urn at a given time representing the temperature. Each of $2N$ balls are numbered and distributed in an arbitrary manner in the two urns (an unequal number in the urns represents unequal temperatures). A number between 1 and $2N$ is selected at random and the ball so numbered is removed from its urn and placed in the other. Upon frequent repetition of this operation the model exhibits Newton's law of cooling. As $N \to \infty$ recurrence times also become infinite, while for a fixed N those states close to equilibrium (half of the balls in each urn) have a small Poincaré cycle, those far from equilibrium having very long ones. These results showed that Poincaré cycles are not incompatible with "practical" irreversibility. Schroedinger & Kohlrausch (4) showed that the urn model is equivalent to the Brownian motion of an elastically-bound particle. The model has been generalized to a continuous one by Siegert (5) and the mathematical theory discussed at some length by Kac (6), Friedman (7), and Bellman & Harris (8). These papers contain many useful techniques of the theory of random processes.

To date no one has succeeded in deriving the laws of nonequilibrium phenomena from the equations of motion merely by allowing the number of particles involved to become infinite. However, considerable success has been achieved by introducing various statistical hypotheses. The admission of a lack of detailed microscopic information in these hypotheses then leads to irreversibility.

Types of Nonequilibrium and Transport Processes

In this section we shall, through examples, survey various types of nonequilibrium processes and the statistical hypotheses used to discuss them. One frequently divides a system into two parts, with the first much larger than the second and in an equilibrium state, and the second in a preassigned nonequilibrium state. One then determines the expected manner in which the second relaxes to its equilibrium configuration in contact with the first by averaging over all phases of the first with their appropriate ensemble weight.

The theory of the Knudsen gas, a gas of low density whose mean free path is large compared with the dimensions of its container, follows this pat-

tern. The walls of the container are postulated to be at equilibrium at a particular temperature. All energy transfer is assumed to occur at the walls. An accommodation coefficient, α, is introduced as the fraction of molecules absorbed and re-emitted at the wall temperature. The remaining molecules are assumed to be reflected from the walls with their original velocity distribution. One can estimate the time required for the gas to come to equilibrium with the walls. Wang Chang & Uhlenbeck (9) investigated the heat transport through a Knudsen gas from a plate at temperature $T+\Delta T$ to one at temperature T with a given accommodation coefficient. They have also generalized their results to gases of higher density where molecular collision also becomes important. Kramers (10) and Payne (11) have discussed the temperature jump and velocity slip at the wall of a container.

In the Lorentz (12) theory of electrical and heat conductivity of metals, the free electrons in a metal execute a random motion in the absence of an external field while the positive ions are postulated to be at rest. The application of an external field organizes the motion to form a current. The velocity achieved by an electron in a given time, and hence the current, depends on the time between the disorganizing influences of electron–positive ion collisions. The collision problem is essentially that of the scattering of small particles from a matrix of fixed larger ones. A hard sphere model was used for both electrons and positive ions and the interaction between electrons was neglected. Lorentz solved the Boltzmann equation (see next section) for this process and found both the electrical and heat conductivity to be proportional to the mean free path of an electron. According to more recent quantum mechanical calculations (see section on quantum fluids) this mean free path is of the order of several hundred lattice distances.

Debye (13) noticed that a thermal gradient could not be set up in a crystal whose vibrations were purely harmonic. He showed (on the basis of a continuum model) that if density fluctuations due to anharmonicities in the thermal motion of the lattice arise, elastic waves are scattered by these fluctuations. A mean free path, λ, of a wave was defined as the distance it could propagate through the crystal before its amplitude was reduced to $1/e$-th of its original value. The thermal conductivity was then given by $\kappa=\frac{1}{3}c\lambda v$, c being the heat capacity per unit volume, and v the wave velocity. This formula led to κ being proportional to $1/T$ in the temperature range of constant c, in agreement with the early experiments of Eucken.

The processes described above concern entities (say particles or waves) which arrive at a volume element (possibly in momentum or phase space) either through streaming or as a result of collisions with another type of object whose state remains undisturbed by the collision. The transport equations for such processes are generally linear integral differential equations. The kernel gives the probability of the object of interest being "scattered" from one specified state to another in a short time. Other examples are the diffusion of neutrons in solids and radiative transfer in gases. The possibility of capture adds an extra term to the transport equation. The considerable

mathematical literature on these multiple scattering processes has been reviewed by Marshak (14), Lax (15), Chandrasekhar (16), and Kourganoff (17).

The concept of mean free path has been fruitful in the discussion of many of these problems. However, it becomes inappropriate when the duration of the collision (temporary capture) is not short compared with the time between collisions. Holstein (18) discusses an interesting example of this, the imprisonment of resonance radiation in a container of gas. Resonance radiation is that emitted by atoms in an optical transition from an excited to a ground state. Such radiation is readily absorbed by other neutral atoms so that no assurance exists for an emitted quantum to reach the walls of the container. An eventual escape may require an enormous number of transfers. While the half-life of an atomic excited state is $\backsim 10^{-8}$ sec., the transit time between collisions of a quantum traveling with the speed of light is considerably smaller.

The Brownian motion of a large particle suspended in a liquid is, according to the theory of Einstein, a consequence of a large number of collisions with the small molecules of the liquid. In a short time interval many collisions occur with molecules moving in all directions so that the average force acting on the large particle is zero. It is only through small instantaneous fluctuations from equilibrium that the large particle changes its state. The Brownian motion is typical of those processes in which some variable undergoes a random variation in such a way that the probability of a large change in a short time is small. The transition probability $P(x, y; t)$ which gives the probability of a transition of the variable of interest from x to y in time t, is then small when $x-y$ is large and t is small. If, in addition, $P(x, y; t)$ satisfies the Smoluchowsky-Chapman-Kolmogoroff equation

$$P(x, y; t) = \int P(x, z; t - \tau)P(z, y; \tau)dz \qquad 1.$$

then the entire process can be discussed in terms of the appropriate solution of the Fokker-Planck differential equation for $P(x, y; t)$. The only information needed is the first and second moments of $P(x, y; t)$ as $t \to 0$ and the initial distribution of the variable of interest. The two standard expositions of this theory are those of Chandrasekhar (19) and Wang & Uhlenbeck (20). Processes which satisfy equation 1 are generally called Markoff processes.

The thermal noise in an electric circuit is analogous to Brownian motion. Fluctuations in the random component of the motion of electrons in a conductor induce a random voltage across the ends of the conductor. Its statistics was analyzed by Nyquist (21) who noted that the electromagnetic energy in a transmission line is distributed into its normal modes according to the classical equipartition theorem (and Planck's law at high frequencies). He showed that if voltage fluctuations were decomposed into periodic components, the spectrum would be $G_v(f) = 4RkT$, R being the resistance of the conductor (with kT being replaced by the Planck formula at high frequencies).

The equation of motion of a Brownian particle (Langevin equation) of

mass m is $m\dot{v}+\eta v = F(t)$, v being its velocity, $F(t)$ the random force acting on it, and $-\eta v$ the viscous frictional force which damps its motion. If v is replaced by a current i, m by an inductance L, η by a resistance R, and $F(t)$ is interpreted as a random voltage, the Langevin equation becomes the equation for the random current in an RL circuit with thermal noise. An RLC circuit corresponds to a Brownian particle in a harmonic field.

Rice (22), in his theory of shot noise (the result of fluctuations in the emission rate of electrons in a vacuum tube) and other fluctuation phenomenon in electrical networks, developed a formalism which has been applied by Wang & Uhlenbeck (20) to Brownian motion type problems. A random function $y(t)$ can be described either through its correlation function $\phi(\tau) = \langle y(t)y(t+\tau)\rangle_{av}$ (the average may be considered to be a time average) or its spectral density function $G(f)$ which is related to $\phi(\tau)$ by the Wiener-Khinchine equation

$$G(f) = 4\int_0^\infty \phi(\tau)\cos 2\pi f\tau d\tau \qquad 2.$$

If $y(t)$ is a random current, $G(f)df$ can be shown to be the power dissipated by a one-ohm resistance in the frequency range $(f, f+df)$. If $y(t)$ has a rapidly vanishing memory, $\phi(\tau)$ diminishes to zero rapidly as τ increases. On the other hand, if $y(t)$ is periodic with a period τ_0, $\phi(\tau)$ has maxima at τ_0, $2\tau_0$, $3\tau_0$, $\cdots$. A narrow $\phi(\tau)$ corresponds to a broad spectral density function $G(f)$. When the statistics of the random force $F(t)$ in the Brownian motion problem is known, one can find the spectral density of the velocity distribution from the Langevin equation and deduce the velocity statistics (20).

We shall discuss the recent generalizations of Brownian motion and Nyquist's theorem in the last section of this paper. The application to noise problems in electrical circuits is reviewed by McCombie (23).

The theory of Brownian motion led Wiener (24) to a function space integral (the so-called Wiener integral) which gives the average value of a functional over all possible Brownian motion paths that connect two given points. It is expected that such integrals and their generalizations will appear more frequently in statistical mechanical and quantum mechanical problems. A general discussion of these integrals can be found in papers by Kac (25) and Montroll (26). Feynmann (27) uses Wiener integrals in his theory of liquid helium and has constructed a similar integral (28) for his approach to quantum theory. The mathematical theory of random processes is well presented by Doob (29), while many physical examples are outlined by Moyal (30).

The statistical hypotheses of the kinetic theory of gases are (*a*) the probabilities of triple and higher order collisions between molecules in rarified gases are negligibly small and, (*b*) the joint probability of finding two particles in two preassigned volume elements in phase space is the product of their independent probabilities of being found in the same two regions. Hypothesis (*b*) is frequently called the molecular chaos hypothesis. This statistical model leads to a nonlinear integral differential equation which is first order in time (the Boltzmann equation). The nonlinearity is a consequence of

(*b*). The Boltzmann H-theorem which implies the statement that the entropy of a rarified gas never decreases, follows directly from the Boltzmann equation. The entropy remains constant when the Maxwellian velocity distribution has been established.

An important type of transport process whose theory is still in a very primitive state is the equilibration of different kinds of degrees of freedom. Since rotational, vibrational, and translational degrees of freedom all exist in polyatomic gases, Lorentz introduced a special "temperature" for each. One generally expresses the internal energy of such gases as

$$E = E_{\text{trans}}(T) + E_{\text{vib}}(T_v) + E_{\text{rot}}(T_r) + \cdots$$

where $T = T_v = T_r$ only at equilibrium. Landau & Teller (31) defined a vibrational relaxation time τ for a diatomic gas by

$$\frac{dE_{\text{vib}}(T_v)}{dt} = \frac{1}{\tau}\{E_{\text{vib}}(T) - E_{\text{vib}}(T_v)\}$$

The experimental importance of vibrational relaxation in gases was first realized by Herzfeld & Rice (32). They noted that the observed increase in sound velocity of air and CO_2 as a function of frequency could not be explained on the basis of the classical Kirchoff theory. They then suggested that "a slow rate of exchange between external and internal degrees of freedom keeps the internal degrees from taking up the whole amount of heat, and, therefore, acts as if the effective specific heat were decreased, and the velocity of sound increased with increasing frequency." Herzfeld and Rice also introduced the concept of the relaxation time τ as a measure of the rate of exchange of external and internal degrees of freedom. Measurements by Pierce on CO_2 led to a value of τ of about 2.6×10^{-8} sec.

There is spectroscopic evidence that vibrational, rotational, and translational temperatures of gases also differ in flames and gaseous discharges [see for example Broida & Schuler (33); Penner (34) who discusses the theory of these processes has criticized the experimental work]. Qualitatively the relaxation time in gases depends on the number of collisions per second and the mechanism of the energy exchange process on collision. The details of the energy exchange are difficult to determine. Some progress has been made in the theory of vibrational relaxation by Schwartz, Slawsky & Herzfeld (35).

An interesting prewar review of the effect of relaxation of various degrees of freedom in gases on chemical activation was prepared by Oldenberg & Frost (36). Herzfeld (37) has also discussed relaxation processes in gases.

Sound absorption and dispersion measurements have played a major role in the investigation of relaxation processes in gases. A review of early work was given by Richards (38). More modern ultrasonics techniques permitted Stewart (39) to observe rotational relaxation effects in H_2 for the first time. The relaxation time varies from 1.65×10^{-8} sec. to 2.48×10^{-8} sec. at 3.855 Mc. as the pressure varies from 1 to 0.5 atm. On this basis about 270 collisions are required for equilibrium to be established.

Kantrowitz (40) investigated vibrational relaxation times by the rapid

compression of a gas at an impact tube. Huber & Kantrowitz (41) measured the relaxation time of several gases by this method. In particular, they found the rotational heat capacity lag in H_2 to imply that 159 collisions are required for the rotation and translation to come to equilibrium at 1 atm. and 12° C., and that of N_2 to require at most 7 collisions. Greene, Cowan & Hornig use their measurements of the shock thickness in a shock wave of N_2 to estimate that about 20 collisions are required to achieve equilibrium (42).

High frequency sound dispersion measurements have been made in liquids to elucidate relaxation effects, but to date no satisfactory theory exists. Experiments by Litovitz & Fox (43) on glycerol give a much smaller sound absorption and dispersion at high frequencies than is expected on the basis of Stokes' theory (using the experimental values of the viscosity in the equations). Kittel (44) has given a discussion of theory of propagation of sound in liquids in his general survey paper on "Ultrasonics Research and the Properties of Matter."

Relaxation effects associated with dielectric and magnetic materials in external electric and magnetic fields have long been a source of information on atomic and molecular processes. An electric field induces a polarization through molecular deformation and the reorientation of permanent dipoles. The deformation effects are temperature independent while reorientation becomes more difficult at lower temperatures.

The temperature independent absorption and dispersion (which is strongest in the optical range) was first discussed through the Lorentz's (12) harmonically bound electron model of an atom, the absorption being strongest at the resonant frequency. Quantum mechanical calculations (45) based on the current atomic model lead to results similar to those of Lorentz.

Debye (46) discussed the temperature dependent relaxation of polar liquids. He considered spherical polar molecules immersed in a viscous fluid, and calculated the frictional torque which opposes the following of the variation of an external field by the dipoles.

Kauzmann (47) has shown that Debye's results can also be derived from a chemical activation model in which he assumes that a molecule goes from one orientation to another only after receiving sufficient rotational energy through collisions to go over a potential barrier. Once the transition probability for going from one state to another is given, the resulting integro-differential equation which describes the relaxation process is similar to those discussed earlier in this section. In the weak collision case the transitions are analogous to those in Brownian motion; if strong collisions predominate, the process is more similar to the Lorentz theory of electrical conduction. Kauzmann discusses the temperature dependence of the transition probabilities by the Eyring theory of absolute reaction rates.

Van Vleck & Weisskopf (48) point out that collision broadening of a nonresonant spectral line is analogous to dielectric relaxation. Since a nonresonant line may be interpreted as a resonant one at zero frequency, they feel that the Debye theory should be the zero frequency limit of that of Lorentz.

They reexamine the Lorentz theory and note that after each collision between molecules the Boltzmann statistics favor orientations with lower energies in the field (Lorentz postulated an unpolarized state on the average after collisions). When they postulate a mean time τ between random collisions, a unification of the Debye and Lorentz theories results from this argument.

The field of dielectric relaxation is well reviewed in books by Frölich (49) and Böttcher (50). Kirkwood & Fuoss (51) have investigated the dielectric relaxation of a system of dipoles with many degrees of freedom such as a linear polymer with many polar groups. The relaxation is described better through a large number of relaxation times than through the single one of the Debye theory.

Insufficient space prevents us from reviewing the important field of magnetic resonance at microwave frequencies here. However, we mention Bloembergen's (52) investigation of spin-lattice relaxation by this technique to emphasize the effect of impurities on relaxation times. While the thermal contact between two kinds of degrees of freedom may be weak (and hence relaxation time long), energy exchange between some degree of freedom in an impurity and the two of the main system might be rapid. The rate of exchange of energy between a system of nuclear spins in a strong magnetic field and lattice vibrations is accelerated by a factor of 10^6 in the presence of paramagnetic impurities. Bloembergen measured the relaxation time for proton resonances in aluminum alum and other salts as a function of carefully controlled chromium impurity concentration and temperature. The relaxation times decrease from 100 sec. to 0.01 sec. with increasing temperature while the theoretical values as given by the Waller and Heitler and Teller formulae for pure salts would range from 10^{10}–10^{20} sec. Bloembergen also shows that the relaxation process follows a diffusion type behavior with sources at the impurities.

We shall now review the recent progress in the general directions outlined above. Lack of space will prevent us from discussing many important irreversible processes such as turbulence, superconductivity, transport properties of liquid He, and absolute reaction rates.

Transport Properties of Gases

The kinetic theory of gases has again become a subject of active research interest, after a long period of neglect in favor of the quantum theory. Part of this new interest has been stimulated by the growing technological importance of high speed, high altitude aerodynamics (superaerodynamics). At altitudes of 100 miles the mean free path, being of the order of 10 feet, is comparable with the size of objects that might attain such heights; at 50 miles it is of the order of the so-called boundary layer thickness. The study of drag and heat transfer of high speed missiles in rarified atmospheres must be based on the kinetic theory rather than on classical hydrodynamics. Some discussion of these problems has been made by Sanger (53) and more recently by Tsien (54), Stadler (55) and collaborators, and Folsom, Schaaf and col-

laborators (56). A low density supersonic wind tunnel has been constructed at the University of California to study the flow of rarified gases around bodies at high velocities [see Schaaf, Hornig & Kane (57)]. A torsion balance for the measurement of forces on objects small compared to a molecular mean free path was developed by Estermann & Kane (58) for use in the wind tunnel.

Various chemical questions arise from superaerodynamics. The process of molecular dissociation is important at surfaces moving with high velocities. The mechanism of dissociation of N_2O_4 in shock waves has been investigated by Carrington & Davidson (59).

The propulsion processes used in high speed missiles have generated new interest in the chemistry of flame propagation and combustion and in the relaxation of various degrees of freedom. The reports of combustion symposia (60) and a review by Evans (61) show the directions of progress in this field.

The phenomenological theory of the condensation of gases has been re-examined from the point of view of the prevention of condensation of vapors in high Mach number wind tunnels. The classical theory is that of Becker & Doering (62). An account of recent work is given by Corner (63) and Gilmore (64). Careful experiments on wind tunnel condensation have been done by Buehler & Nagamatsu (65).

Experimental work on the viscosity and drag coefficients of rapidly moving bodies in rarified gases has been done by rotating a cylinder at high velocities inside a fixed cylinder. Kuhlthau (66) has used a Beams-type ultracentrifuge to drive the inner cylinder in the range of 400 to 1200 r.p.s. with the pressures between the cylinders from 0.5 to 30 microns.

The thermodynamic properties of gases and liquids can be discussed in terms of molecular distribution functions. The n-th of these, $f_n(r_1 \cdots, r_n; p_1 \cdots, p_n)$ (r represents a position and p a momentum vector) in a system of N particles is defined so that $f_n(r^n, p^n)d^{3n}rd^{3n}p$ is the probability of finding any set of n particles in the volume element $dr_1 \cdots dp_n \equiv d^{3n}rd^{3n}p$ at the point (r^n, p^n) of $6n$ dimensional space. Since

$$(N-n)!f_{n-1}(r^{n-1}, p^{n-1}) = \int f_n(r^n, p^n)d^3r_n d^3p_n, \qquad 3.$$

f_n follows from f_N by iteration. Molecular distribution functions of increasingly higher order give progressively more complete descriptions of a system.

The number of particles per unit volume at r at time t, $n(r, t)$ is related to f_1 by $n(r, t) = \int f_1 d^3p$ while the density of a system of particles of mass m is $\rho(r, t) = mn(r, t)$. The mean velocity of a particle is $u(r, t) = [\rho(r, t)]^{-1}\int p f_1 d^3p$ so that the intrinsic velocity is $c(r, t) = \xi - u(r, t)$ where $\xi = p/m$. The average value of c is zero. Certain higher moments of f_1 are also very important.

We write the components of the vector c as c_1, c_2, c_3 (and indeed use an analogous notation for all vectors) and define a set of second and third moments of f_1 by the symmetric tensors with components

$$P_{ij}(r, t) = m\int c_i c_j f_1 d^3p, \qquad S_{ijk}(r, t) = m\int c_i c_j c_k f_1 d^3p \qquad 4a.$$

The contractions[3]

$$\tfrac{1}{3}P_{ii} = p \quad \text{and} \quad \tfrac{1}{3}S_i = \tfrac{1}{3}S_{ijj} \tag{4b.}$$

turn out to correspond to the pressure and heat flux vector while the non-vanishing elements of $p_{ij}=P_{ij}-p\delta_{ij}$ represent the stress tensor. The δ_{ij} vanish unless $i=j$ in which case $\delta_{11}=\delta_{22}=\delta_{33}=1$, $\delta_{ii}=3$.

A detailed analysis of molecular streaming and collisions based on the binary collision and molecular chaos hypotheses leads to the Boltzmann equation for f_1. Its form in a system of identical, spherically symmetrical molecules without internal structure (we drop the subscript "1" on f_1 in the remainder of this section) is

$$\frac{\partial f}{\partial t} + \mathrm{X}_i \frac{\partial f}{\partial \xi_i} + \xi_i \frac{\partial f}{\partial x_i} = J(f) \tag{5a.}$$

where

$$J(f) = \int d^3p_0 \int (f_0'f' - ff_0) g I(g, \theta) d\Omega \tag{5b.}$$

is the rate per unit phase space volume at which particles accumulate at (r, p) due to collisions. The second term on the left of 5a is the time rate of change of f which results from streaming of particles in velocity space while the third term is that due to streaming in position space. Here X_i is the i-th component of the acceleration caused by an external force. Also, $g=|\xi-\xi_0|=|\xi'-\xi_0'|$ where the subscript zero refers to particles which collide with those which are either knocked into or out of a neighborhood of (r, p) of interest. $I(g, \theta)$ is the differential cross section for collision while the integral in equation 5b extends over all momenta $p_0=\xi_0 m$, and over all angles of approach for collision. The primed quantities represent values of the functions after a collision. We shall refer to the Boltzmann equation as BE.

If we identify the variables ρ, u, p, P_{ij}, and S_j with the moments defined earlier, the hydrodynamic equations

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i}(\rho u_i) = 0 \tag{6a.}$$

$$\frac{\partial u_j}{\partial t} + u_i \frac{\partial u_j}{\partial x_i} + \frac{1}{\rho}\frac{\partial P_{ij}}{\partial x_i} = \mathrm{X}_j \tag{6b.}$$

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i}(u_i p) + \frac{2}{3} P_{ij}\frac{\partial u_i}{\partial x_i} + \frac{1}{3}\frac{\partial S_i}{\partial x_i} = 0 \tag{6c.}$$

can be derived from the BE.

In principle, a discussion of any of the dynamical properties of monatomic gases can be based on equations 6 and the equation of state of the gas. However, the exact forms of ρ, p, P_{ij} and S_j are unknown until one solves the BE and employs the moment formulae. Since BE is nonlinear, one usually makes the assumption that the deviation of f from its equilibrium value is sufficiently small that terms quadratic in the deviation can be neglected. In this case BE becomes a linear integro-differential equation in the devia-

[3] We apply the usual summation convention here. Repeated indices imply summation: $P_{ii}=P_{11}+P_{22}+P_{33}$.

tion. The equilibrium f in the absence of external forces is, of course, Maxwellian.

The investigation of transport properties is simplified in either the very low density Knudsen range where it is assumed that the Knudsen number $M = d/\lambda$ (d is the dimension of container and λ is the mean free path) is small or in the relatively high density Clausius range which corresponds to a large Knudsen number. Collisions can, to a first approximation, be neglected in the Knudsen range while streaming is treated as a small perturbation in the Clausius range.

The first real progress toward the solution of the BE was made by Lorentz in connection with his theory of electrical conductivity of metals. This work was extended by Hilbert.

The modern theory of the solution of the BE for particles with an arbitrary force law and for mixtures of particles of arbitrary mass was finally developed by Enskog (67) and Chapman (68). This theory is clearly developed and presented in Chapman and Cowling's book on nonuniform gases (69). We shall refer to this as the CE method.

In the CE method the distribution function is essentially an expansion in powers of the mean free path (and, therefore, appropriate in the Clausius region). The zero-th order distribution function is the Maxwellian distribution. When the various moments of f are computed and substituted into equations 6, one obtains the hydrodynamic equations of an inviscid fluid. In the first approximation for the analysis of a nonuniform gas equations 6 reduce to the classical Stokes-Navier phenomenological equations. The heat flux vector S_j is proportional to the negative of the temperature gradient. Formulae for the proportionality constant, the heat conductivity of the gas, are obtained in terms of the force law. The stress tensor p_{ij} depends linearly on the deformation tensor

$$D_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right),$$

the coefficients being the viscosity coefficient.

The second approximation to the distribution function (qualitatively this corresponds to terms proportional to the square of the mean free path) leads to much more complicated expressions for the heat flux vector and stress tensors. The p_{ij}'s were derived by Burnett (70) and the heat flux vector by Chapman (71) [a slight mistake, which has been corrected by Wang Chang & Uhlenbeck (72) exists in Chapman's expression]. The corresponding approximation to the hydrodynamic equations is called the Burnett equations.

Certain terms have been obtained by Wang Chang and Uhlenbeck for the third approximation. It was learned that with each added approximation one must include more boundary conditions to solve the BE. This is not surprising because each further approximation gives more information about molecular quantities. A detailed discussion of boundary conditions is given in (72) and by Grad (73).

In a new approach to the solution of the BE, Grad represents the distribution function f as the product of the Maxwell distribution function f_0 and an infinite series of "generalized" Hermite vector polynomials (74) in $v = c(kT)^{-1/2}$. Then

$$f = f_0[a^{(0)}H^{(0)} + a_i^{(1)}H_i^{(1)} + \frac{1}{2!}a_{ij}^{(2)}H_{ij}^{(2)} + \cdots] \qquad 7.$$

The first few polynomials are $H^{(0)} = 1$, $H_i^{(1)} = v_i$, $H_{ij}^{(2)} = v_iv_j - \delta_{ij}$ etc. At equilibrium all the a's are zero except $a^{(0)}$, which represents the equilibrium spatial distribution of particles. The Hermite polynomials form an orthonormal set with the weight function f_0. Hence the coefficients $a_{ij}^{(m)} \cdots$ are related to f through

$$a_{ij}^{(m)} \cdots = [1/n(r, t)] \int f H_{ij}^{(m)} \cdots dp \qquad 8.$$

The first few a's are connected to the moments of f by

$$a^{(0)} = 1, \quad a_i^{(1)} = 0, \quad a_{ij}^{(2)} = p_{ij}/p, \quad a_{ijk}^{(3)} = S_{ijk}/p(kT)^{3/2}, \text{ etc.}$$

Hence, in the course of solving BE, one obtains expressions for the tensors of interest in terms of the intermolecular forces.

Grad breaks off the series by retaining terms only up to the third Hermite polynomial. When equation 7 is substituted into the BE with terms retained up to $a^{(3)}$, and with terms quadratic in the a's neglected, a set of differential equations is obtained for the a's or for the hydrodynamic variables ρ, u, T, P_{ij}, S_{ijk}. When he approximates S_{ijk} by a linear combination of its contractions he can discuss all quantities in terms of the thirteen moments of f; ρ, u, T, p_{ij}, and S_i. The equation of state relates ρ and p_{ii}.

Grad briefly discussed heat flow and Couette flow and in the first approximation obtains the Navier-Stokes equations. Higher approximations of the solution of the thirteen-moment equations differ somewhat from the CE solution. Grad believes the complete thirteen-moment approximation yield more reliable hydrodynamic equations than those of Burnett.

Unfortunately, neither the CE nor Grad solutions apply very far from the extreme Clausius range. Convergence of these approximations is slow (and indeed has never been proven) so that it is doubtful that one can proceed very far into the Knudsen range by these methods.

Measurements by Greenspann (74) on the absorption and dispersion of high frequency sound at very low pressures are excellent for the testing of the range of validity of various methods of solving the BE. Originally the velocity and attentuation of 1 Mc. sound was measured at pressures ranging from 0.1 to 30 mm. of Hg. At the lowest pressures reached the wave length was of the order of a mean free path. Experiments are now being conducted at 11 Mc., which, at the lower pressures, correspond to wave lengths much shorter than a mean free path. These conditions are out of the range of even the Burnett equations.

The classical theory of sound dispersion in fluids was developed by Kirch-

off on the basis of the Navier-Stokes equations. The results of this theory are in good agreement with Greenspann's first data if one uses the CE expressions for the heat conductivity and viscosity of Maxwell molecules (those with inverse fifth-power repulsion). The resulting expressions for the dispersion and attenuation are ratios of algebraic expressions in the mean free path divided by polynomials in the same variables.

Wang Chang & Uhlenbeck (75) reasoned that since in the Stokes-Navier approximation the various phenomenological constants are given correctly to only the first power in the mean free path the Kirchoff relations should be expanded in power series in the mean free path and only the linear term retained. As is to be expected this gives a good fit with the data only at the higher pressures. Wang Chang and Uhlenbeck then derive higher order terms in the mean free path and show that the coefficients of increasing powers of the mean free path seem to be increasing. This suggests a very slow or possibly no convergence of the power series expansion.

Truesdell (76) has made a careful examination of the hydrodynamical theory of ultrasonic waves according to the Navier-Stokes equation and given an excellent historical account of the subject. He believes that once it is decided which equation is to be used in the hierarchy of successive approximation one should use the full solution of the equation rather than discard all terms of the same order as those neglected in the derivation of the equation. Examples are known in which the correct qualitative character of the solution of a differential equation is lost if one is too diligent in retaining only terms up to a given order at every step.

Since disturbances from equilibrium have a small amplitude in experiments on sound dispersion, the CE analysis can be simplified considerably. Wang Chang & Uhlenbeck (75) do this by expressing their solution of the BE as a linear combination of the characteristic functions of the linearized collision operator $J(f)$ (see equation 5b). They also emphasize that two parameters, the scale of a disturbance (which might be measured in units of the mean free path) and the intensity of the disturbance should be considered separately. The CE solution mixes these quantities together.

Experiments by Hornig, Cowan & Greene (42, 77) on the determination of the thickness of the shock front in a gas, yield another type of data to be analyzed through the BE. Shock fronts are generally idealized as discontinuities in density, pressure and temperature. However, the molecular nature of gases precludes the possibility of a perfect discontinuity and suggests that a shock front should be spread over at least one mean free path. Even in a continuous material heat conductivity and viscosity would tend to broaden a shock front. Hornig has found conditions under which a shock front should be spread over a distance of the order of the wave length of visible light. Under such conditions the optical properties, and in particular the reflectivity, should be sensitive to the shock thickness. Cowan & Hornig (77) have derived formulae for the shock thickness in terms of the reflectivity for several shapes of shock fronts.

These workers generated shocks in the usual manner by bursting a copper diaphragm in a shock tube. The ratio of the bursting pressure to the pressure ahead of the shock wave was generally kept in the ratio of 3.41. As the low side pressure varied from 40 to 80 lbs./in.^{2} in nitrogen the shock thickness varied from 3.2×10^{-5} to 1.8×10^{-5} cm.

The modern theory of the shock profile and shock thickness was started by Becker (78) and based on the Navier-Stokes equation with a constant heat conductivity and viscosity. The shock thickness predicted by this theory was too small. Thomas (88) improved the calculations by taking into account the temperature dependence of these quantities. The higher approximations of the solution of the BE [Wang Chang (79); Grad (80); and Broer (81)] have been applied to the investigation of weak shocks. Gilberg & Paolucci (82) have made extensive calculations of shock profiles based on the Navier-Stokes equation. So far, the experimental results are not sufficiently accurate to distinguish decisively between the various theories.

Mott-Smith (83) has obtained an approximate solution of the BE for strong shocks. The CE and Grad theories yield skewed Maxwell velocity distributions with a single peak. However, in shock waves, molecules collide in the shock front from both sides of the front, and hence have different Maxwell distributions. On this basis Mott-Smith has used a "best fit" scheme for solving the Boltzmann equation by writing the velocity distribution function in the collision integral as a sum of two Maxwell distributions. He then solves the BE by calculating the collision integral appropriate to such a distribution. The shock front calculated by this method is thicker than that obtained from other schemes.

Shock waves are now being used extensively for the investigation of thermodynamic and relaxation processes in gases as well as in the study of gas reactions. A description of the construction and operation of a typical shock tube has been given by Bleakney, Weimer & Fletcher (84). Hornig (85) has measured the dissociation energy of F_2 by means of measurements of the detonation velocity of hydrogen-fluorine mixtures. He has also investigated free radical formation in CH_3I in a shock front.

Michels, Slawsky & Jacobs (86) [see also Seigel (87)] have developed an interesting rapid expansion procedure for the investigation of the thermodynamic properties of dense gases. The expansion rate measuring apparatus is essentially a hollow cylinder, open at one end, in which a piston may be fixed in an arbitrary initial position. Gas of known volume, pressure, and temperature is introduced in the closed region and the piston released. The thermodynamic properties of the gas can be deduced from the position-time curve of the piston, which is recorded. The theory of the apparatus is the inverse Lagrange problem of the motion of the projectile in a gun. In the Lagrange problem the speed of the projectile is deduced from the properties of the gas which results from the explosion.

The Chapman-Enskog theory has also been applied to the investigation of gas mixtures. The diffusion of one species through another is of consider-

able interest. Maxwell derived Fick's law for gas mixtures and found an expression for the diffusion constant in terms of molecular forces. He accidently missed discovering the phenomenon of thermal diffusion. This phenomenon may be described as follows: if a temperature gradient is maintained in a gas mixture a diffusion will develop with one constituent moving toward the hotter region and the other toward the cooler. In a closed vessel, a stationary concentration gradient exists such that the tendency of ordinary diffusion to promote a uniform distribution just balances the contrary tendency of thermal diffusion.

The thermal diffusion coefficient of a gas with an intermolecular repulsive force proportional to the inverse r-th power of the distance between molecules, has a thermal diffusion coefficient proportional to $(r-5)/(r-1)$. Since Maxwell's calculations on transport phenomenon were mainly restricted to the case $r=5$ he did not realize the possible existence of thermal diffusion. It was discovered by Enskog, and independently by Chapman (who discussed it at great length). An interesting account of the history and present states of the theory of thermal diffusion has recently been prepared by Chapman (89). Hirshfelder *et al.* (90) have done an enormous amount of calculation on the various transport parameters as well as equilibrium properties (including intermolecular force laws) of many gas mixtures. The results of these calculations are included in an exhaustive treatise (90). Practically all significant research recently done on the chemical and physical properties of gases is reviewed in this book (some new proofs and original work of Hirshfelder and his colleagues are presented for the first time). An important treatise on diffusion in all states of matter has been written by Yost (91).

Thermal diffusion has been used frequently for isotope separation. A review of this field and isotope separation in general has been given by Furry & Jones (92) and Cohen (93). A more popular discussion has been made by Peierls (94) and one from more of an engineering point of view by Benedict (95). One of the complicating features of calculating the nonstationary operation of separate processes for binary mixtures (including isotopes) is the fact that these processes are generally described by nonlinear partial differential equations. Some progress has been made in solving these equations exactly by Majumdar (96), Montroll & Newell (97), and Klemm (98). It is interesting that the technique used by Majumdar for linearizing these equations by making an appropriate transformation was used independently by Hopf (99) for the investigation of Buerger's model of turbulence, and by Cole for an analysis of one-dimensional shock waves (100). It has also been applied by Stockmayer to the theory of moving concentration boundaries in electrolytic cells (101).

The kinetic theory of ionized particles is directly applicable to problems of plasma oscillations in discharge tubes, conduction processes in stars, electrical properties of metals, magnetohydrodynamics, the behavior of the solar atmosphere, propagation of radio waves in the ionosphere and their reflec-

tion from ionization trails left by meteors, and chemical reactions in gaseous discharges.

While direct collisions play the dominant role in the energy transfer of neutral gas molecules in the Clausius range, the long range character of the Coulomb forces between charged particles causes a large number of repeated weak interactions which may be more significant, especially at low pressures.

Although high pressures are required to transmit undamped waves in a medium composed of neutral particles, the long range Coulomb forces make it possible to propagate waves (the so-called plasma oscillations) in ionized media or systems of electrons at very low densities. Even in slightly ionized gases the charged particles play a more important role than their numbers would indicate.

The general formulae for the viscosity, heat conductivity, and diffusion in the CE theory, when specialized to an inverse r-th power force law involve certain integrals with respect to the distance between asymptotes to the relative paths of colliding molecules. When $r \geqq 5$ as is the case for neutral molecules, the forces are short ranged. Hence, for mathematical convenience the upper limit to this distance can be chosen to be infinite even though one can hardly consider molecular-pair configurations with greater than an average separation distance to be binary encounters. In the case of Coulomb interactions, the integrals diverge when the infinite upper limit is used. Chapman (102) reasoned that molecular encounters could be considered binary for approaches of less than the average intermolecular distance, but for large distances the intermingling of positive and negative charges might be considered as nearly cancelling their actions on the particle of interest. By taking the mean intermolecular distance as the upper limit of the integrals mentioned above, Chapman obtained results for transport quantities which were not sensitive to the values of the distance chosen (the dependence being logarithmic). Persico (103) followed the Debye-Hückel theory of electrolytes, and used a shielded Coulomb force to derive results essentially the same as Chapman's.

It is to be noted that long range effects are probably not given sufficient attention in this type of calculation. Cohen, Spitzer & Routly (104) have analyzed these by assuming that when the charged particles interact, their velocity distribution is affected by many small deflections produced by many weak distant encounters. By using Brownian motion arguments a Fokker-Planck type of equation was derived to determine the influence of these encounters.

Unfortunately, the Cohen-Spitzer-Routley theory treats distant charges as being independent while correlations are actually very important, as is exhibited through organized motions which involve many charges.

Vlasov (105) considers distant charges to give rise to an effective electromagnetic field which acts on the particles of interest, and incorporates this effective field into the BE in the velocity streaming term. The electromagnetic field must, however, be consistent with Poisson's equation when the

charge distribution is derived from the solution of the BE. A self-consistent-field type of problem then results. Vlasov's formulation is probably the best that one can make without introducing higher-order collision into the BE. Unfortunately, the mathematical development of this scheme is extremely complicated.

Bhatnager, Gross & Krook (106) have simplified the CE development (including the Vlasov approach) by approximating the collision integral in the BE by another integral which still indicates conservation of energy and momentum in the collision process, but which leads to a more tractable equation.

Bohm & Gross (107) and Bohm & Pines (108) have investigated the behavior of ionized media by neglecting binary collisions and examining the collective effects of long range interactions. They start with the classical equations of motion with coulomb interactions between the particles. The particle density function is then Fourier transformed, and a new set of equations of motion is obtained with the Fourier coefficients as variables. A certain random-phase approximation is made to linearize these equations. The authors find a generalization of the Langmuir-Tonks dispersion relation for plasma oscillations. It is found that phenomena which spread over distances greater than the Debye length (the screening radius of the Debye theory of electrolytes) are dominated by collective charge particle behavior, while shorter ranged effects are dominated by simple collisions.

The motion of charged particles in external fields has been investigated through the BE by Wannier (109) and Kihara (110). The electrical behavior of ionic solutions is influenced as much by Brownian motion of the ions as by long range coulomb interaction (111).

Transport Properties of Dense Gases and Liquids

It is generally assumed that the intermolecular potential energy function in gases and liquids is well approximated by a sum of pair interactions $V(r_1 \cdots, r_N) = \Sigma_{i>j} V(|r_i - r_j|)$, $V(r)$ being the potential energy of interaction of a pair of isolated particles separated by a distance r. In this case both the thermodynamic and transport properties of a fluid are expressible in terms of f_1 and f_2.

The theories of Kirkwood (112) and Born & H. Green (113) start with Liouville's equation, the equation of continuity in phase space, for f_N. Integration of Liouville's equation yields the hierarchy of equations

$$\frac{\partial f_n}{\partial t} = [H_n, f_n] + \int\int d^3r_{n+1} d^3p_{n+1} \sum_{i=1}^{n} [V(r_i - r_{n+1}), f_{n+1}], \quad n = 1, 2, \cdots, N \quad 9.$$

$[g, f]$ represents the Poisson bracket of g and f. H_n is the Hamiltonian of n particles. The consequences of the equilibrium form of these equations were discussed by Mayer in the 1950 number of these Reviews (114).

The equations of motion of a fluid follow from the equations for f_1 and f_2 in the hierarchy. The stress tensor and heat current are expressed by Kirk-

wood & Irving (115) and McLellan (116) as functions of f_1 and f_2. For example, the stress tensor at r, $\sigma(r)$, is (in systems close to equilibrium)

$$\sigma(r) = -m\int [p/m - u(r)][p/m - u(r)]f_1 dp + \int \frac{(r_1 - r)(r_1 - r)}{|r_1 - r|} V'(|r_1 - r|)f_2 dp_1 dp dr_1 \qquad 10.$$

Terms with higher order gradients appear in a system far from equilibrium. Here $u(r)$ is the streaming velocity at r. The main contribution to the stress tensor in rarified gases comes from the kinetic energy term (the first given above) while the intermolecular forces (through the second term) are responsible for the internal stresses of a dense fluid. The equilibrium values of f_1 and f_2 lead to a vanishing heat current and a stress tensor identical with the isotropic diagonal tensor for the pressure. When deviations from equilibrium are small, the heat current is proportional to the temperature gradient (as is the case in rarified gases and solids), and the off diagonal elements of the stress tensor to the gradient of the velocity (the proportionality constant being the viscosity coefficient).

The hierarchy, being equivalent to Liouville's equation, is completely reversible. Kirkwood's scheme for introducing irreversibility is strongly motivated by the phenomenological theory of Brownian motion. He remarks that macroscopic measurements always involve an average over a time which is short but still long compared to molecular collision times. He then takes short-time averages of the hierarchy and obtains equations for time-averaged molecular distribution functions. These equations are similar to the Fokker-Planck equations for random processes. In particular, the equation for the time averaged f_1 is identical with the Fokker-Planck equation of the phenomenological Brownian motion theory modified slightly to include small temperature and velocity deviations from equilibrium if they exist. Kirkwood's derivation of the Brownian motion equations is the first based on principles of statistical mechanics rather than on a special model. His averaging process is generally applicable to all kinds of systems.

The friction constant ζ is given in Kirkwood's theory by

$$\zeta = (1/6kT)\int_{-\tau}^{\tau} \langle F(0)\cdot F(t)\rangle_{Av} dt$$

where $F(t)$ is the force acting on a Brownian particle at time t and the average $\langle\ \ \rangle_{Av}$ is taken with respect to a canonical ensemble at the temperature T of the system. M. S. Green (117) has calculated ζ by this formula for a Brownian particle in a rarified gas. The results agree with those first derived by Lorentz who used a method in which one makes a detailed analysis of the momentum transfer in collisions of the gas molecules with the Brownian particle. Kirkwood's time-smoothing statistical hypothesis is thus consistent with collision statistics in rarified gases. Kirkwood (112) has derived the Boltzmann equation by time smoothing the equation for f_1 in the hierarchy.

We have mentioned that the kinetic terms give a negligible contribution

to the stress tensor and heat current of a liquid. Hence, the main problem in their determination is the evaluation of f_2 under the proper conditions. It is assumed that deviations of f_3 from equilibrium are negligible. Then the three factors which enter into the determination of the stress tensor and heat current are the intermolecular forces, the equilibrium f_2, and the friction constant ζ (this is the most difficult to calculate). ζ can be represented by $\theta\langle F^2\rangle_{\mathrm{Av}}/6kT$ where $\langle F^2\rangle_{\mathrm{Av}}$ is the equilibrium mean square force on the Brownian particle and θ is a measure of the time in which $F(t)$ and $F(t+\theta)$ become independent of each other. Kirkwood gives a method of estimating this interval by equilibrium phase space averages only. Kirkwood, Buff & M. S. Green (118) use this estimate to calculate the shear viscosity of liquid argon. Their value is within a factor of two of the experimental one. Zwanzig *et al.* (119) have reported a more extensive calculation of both shear and bulk viscosity by using an improved estimate of the friction constant and a more accurate numerical integration of the required equations. Their shear viscosity has a greater deviation from the experimental values than the results of the rougher calculations. Their bulk viscosity is very sensitive to small changes in the equilibrium pair distribution.

Born & H. S. Green employ the superposition principle (113)

$$f_3(1, 2, 3) = f_2(1, 2)f_2(2, 3)f_2(3, 1)/f_1(1)f_1(2)f_1(3)$$

as the statistical hypothesis which introduces irreversibility into the hierarchy (eq. 9) [We have used the symbol j in $f_1(j)$ to represent $f_1(r_j, p_j)$, etc.]. This cuts the chain at the equation for f_2 so that one has to solve a pair of equations for f_2 and f_1 rather than a large set. The simplification is made at the expense of transforming the original linear integral differential equation into a nonlinear one. Born and Green find f_1 and f_2 by a method similar to that used by Chapman and Enskog for solving the BE. They have not yet carried their analysis far enough to compare their results with experimental data.

Prigogine & Klein (120) have examined the mechanism of relaxation of finite sections of an infinite linear chain of coupled oscillators from various initial configurations, with the intention of estimating the validity of the superposition principle. It is found that although this principle is valid for a linear molecular chain at equilibrium, it does not properly describe the behavior of a chain relaxing from a nonequilibrium state.

H. S. Green derives the BE from the hypothesis that the term in the hierarchy equation for f_2 which involves f_3 can be neglected in a rarified gas (the analogue of the Boltzmann hypothesis that triple collisions are rare). Since this equation then becomes Liouville's equation for a pair of isolated particles, its solution is expressible in terms of the solution of the equations of motion of the isolated pair. The detailed Born-Green approach is given in Green's book (121).

Bogolubov (157) has sought solutions of the hierarchy in powers of the concentration. This is analogous to the equilibrium Ursell-Mayer development. The first term yields the Boltzmann equation.

Transport Properties of Quantum Fluids

The first generalization of the BE for the investigation of a quantum fluid was given in Sommerfeld's theory of electrical and thermal conductivity of metals. This work and many other problems in the electron theory of metals is discussed in the Sommerfeld-Bethe Handbuch article (122).

Essentially, Sommerfeld repeated the analysis of Lorentz but as the first approximation to the velocity distribution function he found the Fermi-Dirac rather than the Maxwell-Boltzmann distribution function and computed the collision term (or better the scattering term) as an average over the Fermi-Dirac distribution. His formulae for the conductivity had the correct functional form, but included an undetermined "mean free path," l, as a parameter. The values of l were later calculated by Peierls, Hauston, Nordheim, and Bloch to be of the order of several hundred lattice spacings as was required by experiments [see Seitz (123)].

Uehling & Uhlenbeck (124) then proposed a generalized BE for one component rarified Einstein-Bose and Fermi-Dirac gases. They replaced the classical collision cross section by the appropriate quantum mechanical differential cross sections (the effects of indistinguishability of particles were included). In systems to which the Pauli exclusion principle applied, provision was made to prevent particles from being scattered into already occupied states. The CE method was used to find expressions for heat conductivity and viscosity coefficients.

The quantum mechanical H theorem was derived by Pauli and Nordheim. Pauli & Fierz (125) have made a critical reexamination of this theory.

One might expect a systematic theory of transport properties of interacting particles to start with a quantum mechanical analogue of Liouville equation and to be developed through a set of quantum mechanical phase space (position and momentum) distribution functions. Dirac (126) argued that such distribution functions do not exist because of the impossibility of measuring noncommuting observables simultaneously. Wigner (127) has, however, constructed a "joint distribution function" for position and momentum of a particle. Although this function may be negative, and hence is not a probability distribution, it does have the property of taking the form of a position distribution when integrated over all possible momentum states, and vice versa.

Moyal (128) has developed the theory of the Wigner phase space distribution function and has applied it to quantum statistics. He has also derived a quantum generalization of the Liouville equation.

Irving & Zwanzig (129) have generalized the classical hierarchy through a set of Wigner functions, and have developed the equations of quantum hydrodynamics. Mori & Ono (130) deduce the Uehling-Uhlenbeck equations from the hierarchy for the time-smoothed (following Kirkwood) Wigner functions. The assumption which introduces irreversibility is that at an initial time the Wigner distribution function is given in its free particle form. Mori and Ono then treat the interaction between particles by quantum

mechanical perturbation theory. The differential cross sections of the collision terms are thus determined by the Born approximation (of scattering theory). Their statistical matrix is chosen with the proper symmetry so that indistinguishability of particles is correctly accounted for in the collision process. These authors also discuss the quantum effect of a nonuniformity in the force field or momentum distribution. Their method does not strictly apply to such cases. However, they do point out that in order for the Uehling-Uhlenbeck equation to be valid, the nonuniformities must be large compared with the mean wave length associated with the particles of interest. Since this wave length is of macroscopic dimensions in a condensed Bose-Einstein gas, the Uehling-Uhlenbeck equation is not appropriate for its study.

Mori (131) has generalized this work to electrons in metals by using Bloch rather than free particle wave functions.

The modern theory of heat conductivity, κ, in dielectric solids has been developed by Peierls (132). He considered the quantum theory of energy transfer between normal modes through anharmonicities in the potential energy in a lattice of atoms. He showed that in a perfect crystal, heat conduction at high temperatures is mainly due to the perturbation of two waves by the anharmonicity in a manner in which momentum is not conserved between the resulting wave and the "colliding" waves. This type of energy transfer is called an Umklapp process and leads to the $1/T$ law of Debye at high temperatures. At low temperatures this process gives a contribution to the thermal resistance proportional to $f(T)$ exp. $(-\Theta/2kT)$ where $f(T)$ is a power of T.

Peierls stated that at low temperatures the predominance of long wave length phonons (lattice waves) should lead to thermal resistance by wall reflections. The details of the reflection of lattice waves by boundaries were examined carefully by Casimir (133) who showed that at low temperatures κ should be proportional to T^3 and the smallest length of the crystal (the radius in the case of a sphere and the width in the case of a long crystal with a square cross section).

Pomeranchuk & Blemeno (134) have discussed Umklapp processes in a manner better suited for experimental interpretation. Klemens (135) has derived a combination formula suited for situations in which both Umklapp processes and boundary scattering are important.

Crystals such as HBr, CH_4, and NH_4Cl which have an order-disorder transition have an anomalous heat conductivity, while paramagnetic salts such as potassium chrome alum seem to have a spin contribution to the thermal resistance. Impurities and lattice defects generally contribute as well.

Excellent experiments on the heat conductivity of solids have recently been performed by Berman, Simon, Wilks, and Ziman. A detailed review of the present status of the subject has been written by Berman (136).

The thermal conductivity of metals is largely determined by collisions and scattering of electrons. A review of this field has been given by Olsen

& Rosenberg (137) who, with Mendelssohn and other members of the Oxford group, have made measurements on metals in both the ordinary and superconducting states.

Nonequilibrium Phenomenon and Theory of Random Processes

Callen & Welton (138) have derived a "fluctuation dissipation" theorem which relates the response of a system to a small external disturbance with the random processes of the undisturbed system. He treats systems whose Hamiltonian depends linearly on a small perturbation induced by a driven variation of some external parameter, $V(t)$,

$$\mathrm{H}(x, t) = \mathrm{H}_0(x) + V(t)Q(x). \qquad 11.$$

$Q(x)$ is the generalized force associated with the driven displacement $V(t)$. V might be the position of a wall, an applied voltage, etc.

Guided by the electrical analogy, Callen defines an admittance function $Y(\omega) = g(\omega) - ib(\omega)$ which is the steady-state response of $\langle dQ/dt \rangle_{\mathrm{Av}}$ to a periodic variation of V

$$V(t) = \exp. i\omega t$$
$$\langle dQ/dt \rangle_{\mathrm{Av}} = Y(\omega) \exp. i\omega t.$$

In the electrical case V is the applied voltage while $\langle \dot{Q} \rangle_{\mathrm{Av}}$ is the current. According to the theory of linear systems $Y(\omega)$ for all ω determines the response to any time variation of V. Callen obtains the generalization of Nyquist's theorem

$$G_Q(\omega) = \frac{2}{\pi\omega^2} E(\omega, T) \operatorname{Re} Y(\omega)$$

where $G_Q(\omega)$ is the spectral energy distribution of Q in the undisturbed system and $E(\omega, T)$ is the mean energy of a harmonic oscillator of natural frequency ω at temperature T.

Callen & Welton (138) prove the fluctuation-dissipation theorem by quantum mechanical perturbation theory. An alternate proof is based on the assumption that macroscopic irreversibility is identical with the decay of a random fluctuation (139).

Jackson (140), in an extension of Callen and Welton's work also discusses the imaginary part of the admittance function. Takehasi (141) derived a classical expression for the indicial admittance (response to a sudden impulse) for an arbitrary phase function μ as well as for Q. He relates the response to a sudden impulse to the correlation function $\langle \mu(t)Q(t+\tau) \rangle_{\mathrm{Av}}$.

Weber (142) has used the fluctuation dissipation theorem to investigate the contribution of quantum mechanical zero point energy to random noise in an electric circuit.

Many thermodynamic "forces" such as temperature, concentration, electrical, and chemical potential gradients lead to irreversible flows or "fluxes"; heat flow, diffusion, electrical currents, and chemical reactions. The early phenomenological laws of these processes—the Fourier law, Fick's law, etc.—relate one flux to a given force. However, many examples exist in

which a given flux might result from several forces; concentration and temperature gradients both lead to diffusion (ordinary and thermal).

In general, one can write

$$J_i = \sum_{k=1}^{n} L_{ik} X_k \qquad 12.$$

which states that each of the n forces $X_1, \cdots, X_n$ contribute to the flux $J_i = da_i/dt \equiv \dot{a}_i$; a_i being the deviation from equilibrium of the gross variable associated with the flux. Onsager (143) pointed out that the general theory of fluctuations implies that in a system close to equilibrium the deviation of the entropy from equilibrium can be expressed as a quadratic form in the a's:

$$\Delta S = -\tfrac{1}{2} \sum g_{ij} a_i a_j$$

He then proved that if the force X_k is defined by $X_k = -\partial(\Delta S)/\partial a_k$, and if the a's are even functions of the velocity, then the phenomenological constants L_{ik} are symmetric $L_{ik} = L_{ki}$. These identities are called the Onsager reciprocal relations.

The Onsager proof is based on the principle of microscopic reversibility, the fact that the microscopic equations of motion are invariant under the transformation $t \to -t$. Since no use is made of particular transport equations, the results have the generality of the thermodynamic laws and do not depend on a particular model. The wide range of useful applications of the Onsager relations is known as thermodynamics of irreversible processes and has been discussed by Prigogine (144) and de Groot (145). Casimer (146) classified macroscopic variables as symmetric or antisymmetric under time reversal. Callen (147) has shown the Onsager relations to be a direct consequence of the generalization of his theory which includes several types of driven displacements $V_j(t)$ (generalization of equation 11). Bergmann (148) has derived them in his theory of generalized statistical mechanics.

Irreversible processes whose phenomenological equations are linear and first-order frequently have a natural connection to some Gaussian-Markoff process. Onsager who was one of the first to see this connection, proposed that the probability of a system making a transition which involves the changes $\{\Delta a_j\}$ in an infinitesimal time Δt is proportional to

$$\exp -\frac{1}{2k}\left\{ \sum_{ij} (L^{-1})_{ij} \frac{\Delta a_i \Delta a_j}{\Delta t} - \sum_i X_i \Delta a_i \right\}.$$

Here L^{-1} is the reciprocal of the matrix L of equation 12.

Hashitzume (149) has discussed this proposal along the lines used in the phenomenological theory of Brownian motion. He shows the transition probability T for the set of a's to go from $\{a_i^{(0)}\}$ to $\{a_i\}$ in time t is the solution of the generalized Fokker-Planck equation

$$\frac{\partial T}{\partial t} = \sum_{ij} \frac{\partial}{\partial a_i} L_{ij} \left(\frac{\partial T}{\partial a_j} - \frac{1}{k} \frac{\partial S}{\partial a_j} T \right)$$

which approaches $\delta(a_i^{(0)} - a_i)$ as $t \to 0$.

Onsager & Machlup (150) have derived formulae for the probability of a set of a_j's having a preassigned time variation in terms of function-space integrals which involve the dissipation function

$$\Phi = \frac{1}{2} \sum_{ij} (L^{-1})_{ij} \dot{a}_i \dot{a}_j$$

and the corresponding function of the thermodynamic forces

$$\Psi = \frac{1}{2} \sum_{ij} L_{ij} \mathbf{X}_i \mathbf{X}_j$$

M. S. Green (151) has developed Onsager's ideas from a more microscopic point of view. He supposes the macroscopic variables of interest, $\{a_i\}$ to be functions of the representative point in phase space and asks what the nature of these functions must be in order that their variation be associated with a Markoff process. The tentative answer is that the $a_i(\mathbf{X})$'s, must in some sense, be all the approximate integrals of the motion of the system. That is, the phase point $\mathbf{X}(t)$ which represents the system at time t traverses the hypersurfaces on which the $a_i(\mathbf{X})$'s have constant values so completely before leaving them that time averages may be replaced by phase space averages in the corresponding microcanonical ensemble. Green then derives Fokker-Planck type equations similar to those of Hashitzume for the transition probabilities of the a's. He also derives phenomenological equations for the time variation of the a's. A set of generalized Onsager relations follow from Green's analysis.

Yamamoto (152) has derived Green's equations from the equations of motion after the introduction of several assumptions. Mori (153) has also considered Green's question.

Transition probabilities were introduced into the quantum theory in Einstein's phenomenological theory of the emission and absorption of radiation. This work was given a microscopic mechanical basis through Dirac's time-dependent perturbation theory. The dynamical variables of interest in statistical applications of this theory have generally commuted with each other and with the unperturbed Hamiltonian. In their theory of nuclear induction, Wangsness & Bloch (154) have extended the Dirac theory of time-dependent transition probabilities to macroscopic variables which do not commute.

Cox (155) has used the theory of transition probabilities between quantum states to investigate the viscous forces generated by slowly varying external parameters and to derive the generalized Fokker-Planck equation for Brownian motion.

The first passage time in random processes has been studied by Siegert (156). In the language of Brownian motion it corresponds to the average time required for a particle in a given volume element to arrive for the first time into another preassigned volume element.

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MODERN ASPECTS OF ELECTRODE KINETICS[1,2]

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The kinetics and mechanism of electrode processes has been, until recently, the most neglected part of electrochemistry, while being, perhaps, the most important. During the last few years, however, the amount of experimental work published has increased considerably, although it has not been accompanied by a correspondingly uniform theoretical development.

A general difficulty of the field is the large effect of impurities in the solution and the state of the (solid) electrode surface. This has led to much work being done at dropping mercury electrodes with the consequent neglect of theoretical knowledge of the electrode phase in determining the mechanism of the process.

The importance of the kinetics and mechanism of processes at electrodes lies, not only in the fact that most of technological electrochemistry awaits an understanding of its basis upon their elucidation, but also because it represents a branch of reaction kinetics in which the effect of controlled changes in the energy of activation (i.e., in part, the overpotential) can be accurately observed.

In this paper, attention will be restricted to activation-controlled processes.

GENERAL CONSIDERATIONS

One of the most important trends in recent studies in electrode kinetics consists in deductions of equations connecting current-potential relations, particularly at current densities (c. d.'s) near to the reversible potential, to stoichiometric factors which allow direct elucidation of the rate-determining step (r. d. s.) in the reaction (1 to 10). However, such methods are applicable only when the current density (c. d.) is negligible compared with the limiting current of the reaction, i_L. Under an a. c. field, concentration overpotential is much less than under d. c. and it is possible to relate the capacity and resistance of the electrode reaction, measured under a. c., to its exchange current, (11, 12, 13) thus enabling measurement of the activation kinetics of "fast" or "reversible" reactions.

[1] The survey of the literature pertaining to this review was concluded in January, 1954.

[2] The following abbreviations will be used: c. d., current density; r. d. s., rate-determining step; h. e. r., hydrogen evolution reaction.

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Rate and potential under d. c.—The general electrode reaction

$$pP + qQ^a + ne_0^- \rightarrow rR + sS^{(q(a-n/a))} \qquad 1.$$

may take place through a number of successive reactions, one of which controls its rate. The rate constant for this r. d. s. depends upon the product of the activities of the reactants in the initial state and the free energy of activation between the initial state and that of highest energy (14). Because the activated state, having the highest free energy referred to the initial state, will have also the highest free energy referred to the final state, the same activated state will apply to the reverse, as well as to the forward, reaction of 1.

On this basis, it is possible (9) to give a general evaluation of the rate constants for 1. The standard electrochemical free energies of the initial and final states of the reaction are expressed as functions of the inner potentials of the metal and solution phase from which it is possible to express the electrochemical free energies of activation for 1 in terms of the Galvani potential difference between metal and solution[4] ($\Delta\phi$). Substitution of the standard free energy of activation, $\overrightarrow{\Delta G^0}\dagger$, into the usual expression for rate constant in terms of free energy of activation, $\Delta G^0\dagger$, then gives the electrochemical rate constants $\overrightarrow{k}$ and $\overleftarrow{k}$ for the forward and backward reactions of 1 and there results for the c. d.'s corresponding to $\overrightarrow{k}$ and $\overleftarrow{k}$ (and in the absence of appreciable influence from diffusion):

$$\overrightarrow{i} = \frac{n}{\nu}\kappa\frac{kT}{h}\,a_P^{p'}a_Q^{q'}a_R^{r''}a_S^{s''}\exp.\left[\frac{-\overrightarrow{\Delta G^0}\dagger + \delta + \dfrac{(\beta+\gamma)n\Delta\phi F}{\nu}}{RT}\right], \qquad 2.$$

$$\overleftarrow{i} = \frac{n}{\nu}\kappa\frac{kT}{h}\,a_P^{p''}a_S^{s'}a_R^{r'}a_Q^{q''}\exp.\left[\frac{-\overleftarrow{\Delta G^0}\dagger + \delta - \dfrac{(1-\beta-\gamma)n\Delta\phi F}{\nu}}{RT}\right], \qquad 3.$$

where p', q', r'' and s'' are the orders of reaction of the r. d. s. in the forward reaction, and r', s', p'' and q'' are those in the backward reaction, with respect to the entities indicated; $0<\beta<1$; $0<\gamma<1$; δ is a function of solution composition, ν, the stoichiometric number, is the number of times the r. d. s. occurs when the over-all reaction takes place once; and the other terms have the meaning usually ascribed to them in rate theory.

The cathodic c. d., i_c, is given by

$$i_c = \overrightarrow{i} - \overleftarrow{i}, \qquad 4.$$

and correspondingly for the anodic c. d.,

$$i_a = \overleftarrow{i} - \overrightarrow{i}. \qquad 5.$$

[4] A treatment of the free energy of activation of electrode reactions, in which the variation of the charge on the activated complex during its formation is considered, has also been given (14).

From the equilibrium condition in which $i_c = i_a = 0$ one obtains i_c and i_a as a function of overpotential in the usual way, i.e.,

$$i_c = i_0 \exp. \left[-\frac{(\beta+\gamma)n\eta F}{\nu RT} \right], \qquad 6.$$

$$i_a = i_0 \exp. \left[\frac{(1-\beta-\gamma)n\eta F}{\nu RT} \right], \qquad 7.$$

when $\overrightarrow{i} \gg \overleftarrow{i}$ and $\overleftarrow{i} \gg \overrightarrow{i}$, respectively.

From 6 and 7,

$$\eta = \frac{\nu RT}{(\gamma+\beta)nF} \ln i_0 - \frac{\nu RT}{(\gamma+\beta)nF} \ln i_c, \qquad 8.$$

and

$$\eta = -\frac{\nu RT}{(1-\beta-\gamma)nF} \ln i_0 + \frac{\nu RT}{(1-\beta-\gamma)nF} \ln i_a, \qquad 9.$$

where i_0 is the exchange c. d.

From 8 and 9, any single electrode reaction under the conditions of 6 and 7 (and in the absence of diffusion control) exhibits overpotential as a linear function of log i[5] so long as

$$\frac{\partial\beta}{\partial\Delta\phi} = 0 = \frac{\partial\gamma}{\partial\Delta\phi}.$$

Stoichiometric quantities.—An equation expressing b as a function of ν was first deduced by Potter (7) [cf. Bockris & Potter (8, 10)]. It is an important diagnostic criterion and can be obtained from measurements near to the reversible potential by use of

$$-\frac{nFi_0}{RT}\left(\frac{\partial\eta}{\partial i_c}\right)_{\eta\to 0} = \nu = \frac{nFi_0}{RT}\left(\frac{\partial\eta}{\partial i_a}\right)_{\eta\to 0}. \qquad 12.$$

Measurements of $\partial\eta/\partial i$ at very low c. d.'s may be difficult. Two alternative equations for ν exist. Thus, (9)

$$\nu = \frac{nF}{2.303RT}\left[\frac{1}{b_a} - \frac{1}{b_c}\right]^{-1} \qquad 13.$$

[5] From 8 and 9 the b factor of the Tafel equation is

$$b_c = -\frac{\nu RT}{(\gamma+\beta)nF} \quad \text{and} \quad b_a = \frac{\nu RT}{(1-\beta-\gamma)nF}, \qquad 10.$$

whence

$$\frac{(\gamma+\beta)n}{\nu} = \alpha_c; \quad \frac{(1-\beta-\gamma)n}{\nu} = \alpha_a. \qquad 11.$$

The term α is called the transfer coefficient; β may be called the symmetry factor.

and (8, 10)

$$\frac{n\eta_{s,a}}{0.075} = \nu = -\frac{n\eta_{s,c}}{0.075}, \qquad 14.$$

where η_s is the overpotential at which the Tafel line just commences to deviate from linearity due to the effect of the back reaction.

Parsons (9) showed that the stoichiometric coefficients, p', q', etc., can be obtained from the variation of the c. d. at constant $\Delta\phi$ and in other ways. The simplest relation is obtained when excess indifferent electrolyte is present in the solution, so that $\partial\Delta\phi/\partial \ln a_q = 0$, when,

$$\left(\frac{\partial \ln \vec{i}}{\partial \ln a_p}\right)_{\Delta\phi,T,a_q} = p'. \qquad 15.$$

Analogous expressions can be obtained for the components Q, R, and S so that the other terms similar to p' in 2 and 3 can be obtained. Also, by evaluating the reversible Galvani p. d. corresponding to 1 from thermodynamics and comparing it with the value obtained by equating 2 and 3, it is found that

$$p' - p'' = \frac{p}{\nu}; \; q' - q'' = \frac{q}{\nu}; \text{ etc.} \qquad 16.$$

Thus, knowing ν and p', q' etc., 1, and its rate determining reaction, are known.

Rate and potential under a. c.—Application of Fick's Law to the metal-solution interface under a. c. has been made in a number of cases by Erschler (12). One obtains equations such as[6]

$$R_s = \frac{RT}{zF}\frac{1}{i_0} + R_{d,s} \qquad 17.$$

where R_s is total resistance of the electrode reaction, and $R_{d,s}$ is resistance due to concentration overpotential. Analysis of $R_{d,s}$ shows it to be proportional to $\omega^{-1/2}$, where $\omega = 2\pi\nu$ and ν is the frequency of the a. c. used. So, upon entrapolation to $\omega = \infty$, R_s and i_0 may be gained (e.g., in systems where measurement of i_0 by d. c. is not possible because i_0 is not much smaller than i_L).

This approach can be extended to complex reactions, e.g., those involving formation of an adsorbed layer, and the frequency variation of R_s is characteristic of the rate controlling step [e.g., distinguishes discharge from adsorption, (12, 15) etc.].

Kinetics at dropping mercury electrodes.—Until recently, reactions at dropping mercury electrodes were considered as entirely diffusion controlled.

[6] Thus, this equation would apply to the deposition and dissolution of a metal if the diffusive capacitance and resistance are assumed to be in series in the equivalent circuit for the reaction.

However, Tamamushi & Tanaka (16) and Eyring, Marker & Kwoh (17) independently showed that rate constant and transfer coefficient of a sufficiently slow electrode reaction could be evaluated from polarographic measurements. This theory of reactions under diffusion and activation control at a dropping electrode has been extended by Delahay (18, 19), particularly for oscillographic polarography.

Examination of the mechanism of electrode reactions at a dropping electrode has the advantage that it makes less exacting the limit below which the solution must be purified. Conversely, particularly in organic reactions, the course of the reaction cannot be followed by isolating the products, and the charging current may interfere with measurements at low c.d.'s which are necessary to obtain ν.

Rate and temperature.—Expansion of equations such as 2 in terms of $\Delta H^{0}\dagger$ and evaluation of i_0 leads to the expression (valid when the electrokinetic potential, ζ, is zero),

$$\left(\frac{\partial}{\partial \frac{1}{T}} \ln i_0\right)_{\beta,\gamma,\delta,a_i} = -\frac{\overrightarrow{\Delta H^{0}\dagger} + \delta - \left(\frac{\beta+\gamma}{\nu}\right)\Delta H_R}{R} \qquad 18.$$

where $\Delta H^{0}\dagger$ is the standard heat of activation of the forward reaction when the Galvani p. d. is zero and $\Delta H_R{}^0$ is the change in enthalpy in the reaction under reversible conditions (20). Reaction 18 may be written as

$$\frac{\partial}{\partial \frac{1}{T}} \ln i_0 = -\frac{\Delta H^{0}\dagger}{R}, \qquad 19.$$

and $\Delta H^{0}\dagger$ has been called the "heat of activation at the reversible potential." However, 18 shows that $\Delta H^{0}\dagger$ contains terms of a different nature from a heat of activation. It is therefore better termed a "virtual heat of activation." Little interest is attached to $\Delta H^{0}\dagger$ or the corresponding $\Delta H^{0}\dagger$ because the potential to which they refer cannot be determined (22).

$\Delta H^{0}\dagger$ can also be determined from measurements of c. d. as a function of T at constant overpotential and from the variation of overpotential with temperature at constant current. Reactions for which $(d\alpha/dT) \neq 0$ have also been considered (14a).

The Hydrogen Evolution Reaction

Experimental facts.—The hydrogen evolution reaction (h. e. r.) deserves special attention because much more is known about it than about any other electrode reaction (20, 22). Values of i_0 vary on different electrodes from about 10^{-3} amp. cm.$^{-2}$ to 10^{-13} amp. cm.$^{-2}$ (Hg. $\Delta H^{0}\dagger$ varies between about 5 kcal. mole^{-1} (Ni) to about 21 kcal. mole^{-1} (Hg). Transfer coefficients usually have the values 2 or about 0.5 in pure solutions. Detailed values of the parameters have recently been reviewed (23). The Tafel equa-

tion applies over a range of 10^{11} amp. cm.$^{-2}$, up to 100 amp. cm.$^{-2}$ (24). Log i_0 varies linearly with the work functions of the metal (25).

On metals for which i_0 is low (e.g., Hg), pH has no effect on i_c in acid media up to pH = 1, the rate increasing with decrease of pH in more acid solutions (20, 26). On metals of higher i_0 (e.g., Ni, Pt), this increase begins at a higher pH and effects are sometimes complex [e.g., on Ag (26)]. On Hg, Cu, and Ni, the i_0 in alcoholic acid solutions is 10 to 100 times greater than that in corresponding aqueous systems (27 to 31). The rate depends on the state of electrode surface: anodic activation (32), porosity (33), electropolishing (34), and solidification (35) have been examined. At single crystals, i_0 depends on the face chosen (36). At alloys, it decreases with decreasing solubility of H in the alloy (37). It is independent of p_{H_2} (29).

The h. e. r. is markedly sensitive to trace impurities (38). Sheet electrodes, polarized on one side, exhibit overpotential on the other (isolated) side after a short time (39). For Fe and Pt, the effect is decreased on increased purification of the solution (40).

Kinetics.—When the source of the proton is H_3O^+, probable reactions are (M = metal of electrode):

$$H_3O^+ + e_0^- \xrightarrow{V_1} MH + H_2O \qquad \text{A.}$$

$$MH + MH \xrightarrow{V_2} 2M + H_2. \qquad \text{B.}$$

Or,

$$H_3O^+ + e_0 \xrightarrow{V_1} MH + H_2O, \qquad \text{A.}$$

$$H_3O^+ + MH + e_0 \xrightarrow{V_2} M + H_2 + H_2O. \qquad \text{C.}$$

In these two paths, A, B, or C may be the r. d. s. and mechanisms corresponding to these controls are termed "slow discharge," "atomic hydrogen," and "electrochemical," respectively. Similar mechanisms occur when H_2O is the source of protons. In alkaline solutions, mechanisms involving an alkali metal may take part in the kinetics so that paths such as (41):

$$M_{Alk.}^{+} + ze_0 \rightarrow M_{Alk.} \qquad 20.$$

$$M_{Alk.}^{+} + zH_2O \rightarrow M_{Alk.} + zMH + zOH' \qquad 21.$$

$$zMH \rightarrow \frac{z}{2} H_2 + zM \qquad 22.$$

may occur.[7]

More complex mechanisms occur when (i) simultaneous reactions take place, e.g., two desportive processes proceed with velocities of the same order; (ii) dual reactions occur, i.e., two stages in the h. e. r. have nearly equal energy barriers. The term "linked reaction" may be applied when the energy barriers of successive steps are of different heights but the kinetics of the

[7] Additional reaction mechanisms are given in references (8, 9).

over-all reaction depends on the height of two or more energy barriers. Transitions from one mechanism to another are marked by characteristic changes in b values (42).

The detailed kinetics of the simpler of these steps have been given from a consideration of the stationary state of surface-adsorbed H during H_2 evolution (8). This method [cf. also (9)] leads to the following criteria of the mechanisms of the h. e. r.

TABLE I

CHARACTERISTIC VALUES OF DIAGNOSTIC CRITERIA IN THE HYDROGEN EVOLUTION REACTION

Mechanism	b 25° C., $\beta=\frac{1}{2}$	ν
A slow, B fast	0.116	2
A fast, B slow	0.029	1
A slow, C fast	0.116	1
A fast, C slow	0.038	1
	or 0.116*	1

* Depends on potential (8).

Primary criteria.—The two most important criteria are:

$$(a)\quad \frac{\partial \eta}{\partial \log i} = -2.303\frac{RT}{\alpha F} = b \qquad 23.$$

valid when exp. $[-(\eta F/RT)]>10$; and

$$(b)\quad \nu = -\frac{2i_0F}{RT}\left(\frac{\partial \eta}{\partial i}\right)_{\eta\to 0}. \qquad 24.$$

Values of these criteria corresponding to the paths A—B and A—C are given in Table I. Values of b quoted are approximate on account of the assumption made in their derivation that $\beta=0.5$. Both b and ν are, in general, necessary to decide upon a mechanism but observation of b values of 0.029 or 0.038 determines the mechanism without ν. Note that ν determined from (24) indicates the mechanism only at limitingly low c. d.'s [but cf. (10, 43)].

Secondary criteria.—These are:

(*a*) pH and salt effects. These are used to identify the ion undergoing discharge.[8]

(*b*) Virtual Heat of Activation at the reversible potential. This is of use in making distinctions between mechanisms based on potential energy barrier calculations.

[8] For theory of pH and salt effects and a summary of the results see reference (20).

Mechanism at various electrodes.—The r. d. s. of the h. e. r. may be regarded as having been established without reasonable doubt in the following systems, over the range of conditions in which the diagnostic criteria apply. (*i*) On Hg in alkaline solutions (41), where it is 21, with the probable reaction sequence 20, 21, 22; (*ii*) On Ni (10) and Cu (43) in alkaline solutions, where the r. d. s. is the analogue of A for H_2O discharge, followed by B; (*iii*) On Pt (24) and Pd (44), where at low c. d.'s in acid solutions, the r. d. s. is B, preceded by A.

The r. d. s. can be considered as having been established with good probability in the following systems: On Hg (45), Pb (46) Ni (10), and Cu (43) in acid solutions, the r. d. s. is A and on Ni there is some evidence that this is followed by B.

A b value of 0.04 (Cf. Table I) has hitherto been observed only for Mo in 1 N HCl (31) and for some systems in nonaqueous solutions (31), but in no system under fully satisfactory conditions. The mechanism on Ag is uncertain in spite of work in highly pure systems because the b values at low c. d.'s are between the two values possible for the electrochemical mechanism (26, 47). The principal requirement at present is the establishment of more data in highly purified solutions.

Discussion.—If ν is not known, distinction between A and C as rate determining stages can only be made if the approximate degree of coverage is known, for C with $b=0.116$ is associated with an electrode surface highly covered with it in the steady state (8). The surface tension method of estimating this coverage, suggested by Frumkin (45), is the least indirect method known [but cf. (48)]. The persistence of A as the r. d. s. on electrodes on which there is a high heat of adsorption of H has been related (10) to the fall of the heat adsorption of H found upon increasing the coverage of the substrate (49).

The limiting value of 10^{-10} mol. $l.^{-1}$ found by Bockris & Conway (26) for the concentration of impurities which appreciably affects the velocity of the h. e. r. can be shown to be physically reasonable if these impurities congregate preferentially near the metal-solution interface (22).

The change of one mechanism for the h. e. r. to another has been formulated graphically and mathematically (8, 42). The difficulties of a quantitative calculation of the c. d. at which one mechanism changes to another (50, 51) are increased by the meager knowledge of the potential of a charge-free surface in the solution [but cf. (52)] and of the galvani potential difference between metal and solution. Evidence against mechanisms not discussed here is given elsewhere (20).

Cathodic Processes

Metal deposition.—Particular difficulties which concern metal deposition studies are: (*a*) i_0 is large and it is therefore difficult to distinguish activation and concentration overpotential; (*b*) the true c. d. is difficult to obtain

owing to the tendency in some systems to deposit in certain spots. This can be overcome by microphotography of these areas, and of the growing filaments which sometimes occur (53); and, potentially, by electron diffraction examination and measurement of the emission from a deposited tracer; (*c*) the change of "activity" of the surface with time. In this connection, it was suggested some years ago by Roitar, Juza & Polujan (54) that this difficulty could be overcome by measuring the overpotential at the maximum of the charging curve (potential against time) for various c. d.'s.[9] Few systematic results obtained by this method are available. Few a. c. studies have been made (11, 12). They are sensitive to impurities (55).

Whether the paucity of evidence that the Tafel equation is applicable in metal deposition is due to intrinsic causes [$(\partial\beta/\gamma\Delta\phi)\neq 0$], or to change of the activity of the surface with c. d. and time, is not satisfactorily established, although older work (56) in which secondary effects were avoided shows that linear Tafel lines are then obtained in some systems.[10] Insufficient values of i_0 (20) have been determined to allow quantitative conclusions to be drawn concerning any relation between rate constant and electrode material although it follows qualitatively from the work of Piontelli (64 to 67) that i_0 is high for groups I A and II A and low for transition metals; it increases for a given metal with increase of polarizability of the anion in solution (57 to 60). Conversely, the presence of adsorbable organic molecules in solution decreases i_0 with increase of size (61, 62) (i.e., polarizability).

Two types of r. d. s. are possible: (*i*) ionic transfer (rather than discharge) from the solvation sheath to the metal phase; (*ii*) transfer of an ion from the point of deposition to a point at which it can be accepted into the metal lattice. The rate of the latter process can be determined by (*a*) diffusion across the surface; (*b*) the formation of two dimensional nuclei. If the rate of (*b*) can be regarded as proportional to the c^2_{metal} considerations of the steady-state during deposition (20) show that the b values appropriate to these mechanisms are approximately 2.303 RT/zF and 2.303 $RT/2zF$ respectively, while that for slow transfer from the solution is 4.606 RT/zF. The limited number of b values hitherto obtained (54, 68) indicate the value 4.606 RT/zF and hence support (*i*) as the r. d. s.

On this basis, transition metals have low values of i_0 because cohesion in their lattices is particularly strong on account of their partly filled d zone. Consequently, the energy needed to "break open" the lattice and exchange ions with the solution is particularly high (69). Likewise, the anion effect can be interpreted in terms of the increased negative ζ-potentials caused by the specifically adsorbed (i.e., more polarizable) anions. However, this ex-

[9] The overpotential would then be measured before secondary effects had time to become effective.

[10] Claims of lack of applicability of the Tafel equation in other systems have proved illusionary when the technique of experimentation has been improved.

planation cannot apply above concentrations of 1 N, where the ζ-potential is suppressed, although the anionic effects are still observed (60).

Inorganic Reduction

Diagnostic criteria.—Older experiments by Kobosew & Nekrassow (70) indicated that WO_3 was reduced at a finite distance from an electrode and lead to the conclusion that H must be the primary reducing agent. This, however, is not in accord with a calculation (71) of the number of H atoms escaping through the diffusion layer at an electrode, according to which, e.g., at a hydrogen overpotential of -0.8 v., this is 10^{-4} atoms cm.$^{-2}$ sec.$^{-1}$.[11] Bagotsky & Jofa (71) confirmed this by direct observation on pieces of WO_3, some in contact with the electrode and some at 0.1 mm. away from it, finding only those in contact reduced. Electron transfer is thus the primary stage.

This conclusion cannot be generalized because WO_3 is a good electronic conductor; further, the calculation referred to indicates the improbability of reduction by H at a distance from the electrode but does not concern the effect of H on particles adsorbed on the surface.

The electroreduction of oxygen.—On Hg, Pt, Ag, and Au cathode, $\partial\eta/\partial \log i_c = 0.12$ and on Cu, 0.03 at 25° C. (72, 76). Possible r. d. s.'s are (a) diffusion of O_2 to the electrode surface; (b) adsorption of O_2 on the electrode; (c) reduction of adsorbed O_2, (α) by a process not involving H, (β) by one involving H. At Hg, the reduction occurs in two stages with intermediate formation of H_2O_2 (73). The following mechanism is probable (76):

$$O_2 + H^{\cdot} + e_0^- \xrightarrow{\text{slow}} HO_2 \qquad 25.$$

$$HO_2 + H^{\cdot} + e_0^- \rightarrow H_2O_2. \qquad 26.$$

Hence,

$$i = k a_{H_2O_2} a_{H^{\cdot}} \exp.\left[-\frac{\zeta F}{RT} - \alpha(\Delta\phi - \zeta)\frac{F}{RT}\right], \qquad 27.$$

where ζ is the zeta potential. From 27, if $\alpha = 0.5$, $b = 0.12$ at 25° C., as observed. Equation 27 also accounts for the effect of O_2 concentration on the hydrogen evolution rate at Hg, the only type of this information available (73).

At Cu, the slope of the Tafel line observed accords with the diffusion of O_2 as the r. d. s. The more complex mechanism of the reduction of O_2 on C electrodes has also been discussed (74, 75).

Other systems.—The irreversible reduction of several metal ions has been examined, e.g., Ti^4 (78). Two successive reactions,

$$Ti^4 + e_0^- \rightarrow Ti^{3\cdot} \qquad 28.$$

$$Ti^3 + e_0^- \rightarrow Ti^{2\cdot} \qquad 29.$$

[11] These calculations are inconsistent with the reduction at a distance from an electrode claimed for various metal oxides (77). It appears that accidental contact with the electrode may have occurred in this work.

occur in acid solutions with low i_0 values.

In the reduction of aqueous tungstate solutions in the presence of codepositing metals, such as Fe, Co, and Ni, the over-all reactions occurring are (79)

$$M^{++} + 2e_0 \rightarrow M \qquad 30.$$

$$WO_4'' + 8H^{\cdot} + 6e_0^- \rightarrow W + 4\,H_2O. \qquad 31.$$

Reaction 30 occurs until the cathode is covered with a thin deposit of the metal, M, which then reduces the activation energy for 31 to occur; when the electrode is covered with W, 30 commences again, and so on, so that a laminated surface of M and W are obtained.

The necessity for adsorption of the reactant on the electrode has been demonstrated in certain reductions, e.g., tetrachlorplatinate and persulphate ions, the reduction ceasing at potentials more negative than that of the electrocapillary maximum (80, 81).

Organic Reduction

Diagnostic experiments.—A critical experiment to distinguish between mechanisms of the type

$$H^{\cdot} + e_0^- \rightarrow MH \qquad 32.$$

$$R + MH \rightarrow RH + e_0^- \qquad 33.$$

where R is an organic molecule; and

$$R + e_0^- \rightarrow R' \qquad 34.$$

$$R' + H_3O^{\cdot}\ (\text{or } H_2O) \rightarrow RH + H_2O\ (\text{or } OH') \qquad 35.$$

has been performed by von Stackelberg & Weber (82), who subjected various reducible organic compounds, mainly quinones, to both sides of a Pd plate electrode, on one side of which R was in contact with H and electrons and on the other only with H, obtained by diffusion through the cathode. Reduction was almost entirely on the electrolysis side. It was concluded that for substances with reduction potentials more negative than -0.1 v. (N H scale) at pH$=0$, the reduction mechanism is always by means of primary electron transfer [i.e., (34, 82, 84 to 87)].

In certain other reactions, the nature of the products unambiguously indicates electron transfer as primary (82). Thus, reduction of dibromethane and 2.3 dibromethane at an Hg cathode yields ethylene and butylene respectively. The primary step is therefore of the type

$$RCHXCHXR + 2e_0^- \rightarrow RCH = CHR + 2X'.$$

Had H been the primary additive, a saturated hydrocarbon would result.

Similarly, reduction of the alkyl monohalides at a Hg surface corresponds to the over-all reaction (88).

$$RX + H^{\cdot} + 2e_0 \rightarrow RH + X. \qquad 36.$$

The reaction can be regarded as occurring in three stages

$$RX + e_0^- \rightarrow R + X' \qquad 37.$$

$$R + e_0^- \rightarrow R' \qquad 38.$$

$$R' + H^+ \rightarrow RH \qquad 39.$$

The reaction course, and the fact that the r. d. s. is 37, is supported by the relation between the half-wave potentials for a series of R's and the R–X bond strengths.[12] The relation is approximately linear (the bond strength is clearly not the only factor affecting the energy of activation in 37).

A good example of the elucidation of reaction mechanism by the use of diagnostic criteria analogous to those discussed in the introduction is that for the reduction of quinones (89). At pH <5, the reaction course is

$$Q + H^+ \rightarrow QH^+$$

$$QH^+ + e_0^- \rightarrow QH$$

$$QH + H^+ \rightarrow QH_2^+$$

$$QH_2^+ + e_0 \rightarrow QH_2$$

Effect of electrode material.—Formerly, it was thought that a parallelism existed between the hydrogen overpotential at a cathode and its efficacy in reduction but too many exceptions are now known for this to be accepted (84). Qualitatively, it is clear that the free energy of activation for the reduction reaction depends on the adsorption energies of the reactant and the products on the electrode and these depend on the nature of the electrode (distribution of active sites) and properties of the reactants and products (e.g., size and position of adsorbable groups). The reducing power of a cathode is hence a specific property of the system.

Adsorption kinetics.—Development of equations for the adsorption and diffusion capacitance as a function of frequency of the applied a. c. shows that for a process in which diffusion is rate-controlling, there is a more rapid fall of capacitance with increase of ν at low frequencies than for adsorption control. Hence, it has been established (15) that adsorption of normal aliphatic alcohols on Hg is always rapid compared with their diffusion to the electrode surface.

The rate of adsorption of Cl′ and O onto Hg is much higher than that onto Pt (11, 12). This is probably because adsorption of oxide and halide onto the surface of a metal weakens the interatomic forces between neighboring surface atoms, so that the rate of adsorption would decrease with increasing stability of the metal crystal lattice.

Anodic Processes

The oxygen evolution reaction.—The principal difficulties in the study of this reaction have been that it is limited to noble metals and that the rever-

[12] A detailed discussion of the structural factors affecting carbon-halogen bond fission has been given by Elving (87).

sible oxygen electrode could not be achieved, the Tafel line departing from linearity at a c. d. of about 10^{-6} amp. cm^{-2}. Recently, Bockris & Huq (32) found that if the solution was subjected to prolonged cathodic, and then anodic, preelectrolysis, these deviations disappeared and the Tafel line obeys the theoretical behavior to zero current.

Values of i_0 on Pt are $\simeq 10^{-10}$ amp. cm.$^{-2}$, and α in acid solutions is about 0.5. Results, e.g., for α in alkaline solutions, are not in good accord. Such discrepancies doubtless depend on impurity effects and different initial states of the electrode surface (90 to 94). From pH 0.5–14, i_0 is independent of pH. A number of substances containing S and N decrease i_0 on Pt but the effects do not occur on Au and Pd (92). Addition of dioxan or acetic acid to an aqueous solution decreases α on Pt (95).

Possible paths for the oxygen evolution reaction are more numerous than those for the h. e. r. Some of them are analogous. In addition, it is possible that after discharge of OH′ (or H_2O in acid solutions), the course is (96)

$$2M - OH \rightarrow 2M + M - H_2O_2, \qquad 40.$$

$$M - OH + M - H_2O_2 \rightarrow H_2O + M - HO_2, \qquad 41.$$

$$M - HO_2 \rightarrow H_2O + M + O_2, \qquad 42.$$

or,

$$2M - OH \rightarrow H_2O + M - O \qquad 43.$$

$$M - O + M - OH \rightarrow M - O - OH \qquad 44.$$

$$MO - OH + MOH \rightarrow H_2O + M + O_2 \qquad 45.$$

By consideration of the steady-state during O_2 evolution it is possible to deduce b and ν criteria for all probable paths. On Pt one finds $b \simeq 0.12$ for the anodic evolution and this is found (32) to be in accord with the r. d. s.'s

$$OH' \rightarrow M - OH + e_0; \qquad 46.$$

or,

$$M - OH + OH \rightarrow M - O + H_2O + e_0 \qquad 47.$$

However 40 gives a ν value of four and 47 a value of two, and utilizing 13 and a b value of 0.097 for the cathodic dissolution reaction (32), ν is found to be four. Hence 40, or its analogue with H_2O discharge, is the r. d. s. for oxygen evolution of Pt.

Redox reactions.—Application of kinetic measurements to the determination of redox mechanisms has commenced only recently. In particular, measurements of the dependance of i_L upon the concentration of oxidized and reduced species, and the evaluation of $\partial i_0/\partial \log a_c$ have been shown by Vetter & Manecke (97) to give diagnostic results.

Decrease of the exchange current is observed in redox processes on Hg upon addition of adsorbable anions, e.g., I′, CNS′ (55). Sensitivity to impurities is exhibited, e.g., gelatin reduces redox rates, the effect reaching a constant value as the gelatin concentration is increased, presumably owing to the attainment of a monolayer (55). Organic redox reactions are difficult to

measure because they often involve side reactions. The first-stage reduction of pyocyanin and the first-stage oxidation of tetramethylparaphenylenediamine have been examined. They show abnormal results, probably due to adsorption of products on the electrodes (55).

The mechanism of several simple redox reactions of the type $M^{z}+2e_0 \rightarrow M$ has been examined (97, 98). The r. d. s. is not always identical with the over-all reaction, e.g., for $Mn^{4+}+e_0 \rightarrow Mn$, the r. d. s. is (97)

$$Mn^{3+} + e_0 \rightarrow Mn^{2+} \qquad 48.$$

followed by

$$Mn^{2+} + Mn^{4+} \rightarrow 2\ Mn^{3+} \qquad 49.$$

A less simple redox reaction is that between HNO_3 and HNO_2 where measurements of i_L as a function of c_{HNO_3} and c_{HNO_2} suggests that a chemical reaction involving both acid molecules is rate determining (99). The course suggested is

$$H^{+} + NO_3^{-} \rightleftarrows HNO_3 \text{ (Rapid)} \qquad 50.$$

$$HNO_3 + HNO_2 \rightleftarrows N_2O_4 + H_2O \text{ (r. d. s.)} \qquad 51.$$

$$N_2O_4 \rightleftarrows 2\ NO_2 \text{ (Rapid)} \qquad 52.$$

$$2\ NO_2 + 2\ e_0 \rightarrow 2\ NO_2^{-} \text{ (Rapid)} \qquad 53.$$

$$2\ NO_2^{-} + 2\ H^{+} \rightarrow 2\ HNO_2 \text{ (Rapid)} \qquad 54.$$

$$3\ H^{+} + NO_2^{-} + 2\ e_0^{-} \rightarrow HNO_3 + H_2O \qquad 55.$$

The energy of activation in redox reactions depends largely upon the magnitude of the structural change brought about in the reaction. For example, for ferro ferri oxalate in N/2 oxalate solution, the large ionic size implies a small primary hydration sheath, so that change of charge on the complex brings about a small change in the hydration energy and the resulting activation energy is hence small (55) However, for systems involving, e.g., Y^{3+}, Cr^{3+}, and Fe^{3+}, the change in hydration energy upon change of charge of unity would be considerable; and this is consistent with the observed $\Delta H^{0}\dagger$ value of 7–10 kcal. $mole^{-1}$ in such systems (55).

The anodic oxidation of S has been examined and is complicated by polysulphide formation and by passivity effects connected with the deposited S layer (100). Few other recent studies of anodic oxidation exist (101).

Potential Energy Curves

Older work on the calculation of the potential energy curves for electrode reactions was not of quantitative value because of the inaccuracy of the parameters available. Parsons & Bockris (102) carried out a detailed calculation of the heat of activation and transfer coefficient for proton discharge with particular reference to effect of accuracy of the parameters used on the results obtained. It was found possible to calculate $\Delta H^{0}\dagger$ and β in meaningful agreement with experiment at Hg and Ni cathodes for the h. e. r. Absolute

calculations of i_0 cannot be made with significant accuracy, owing largely to the inaccuracy of the calculations of ΔS^0†.

Such calculations can be applied to verify the physical significance given to the symmetry factor, β,[13] (102) and that for the separation of isotopes. They show that for the h. e. r. it is inprobable that proton discharge occurs from water, compared with H_3O^+, in appreciably acid solutions (102), and that on Cu in alkaline solutions it is improbable that Na^+ discharge occurs compared with proton discharge from water (43). They have also been used to calculate the effect of changing from aqueous to alcoholic acid solutions on the proton discharge rate (27). In these comparative calculations, the ratio of the two rates can usually be obtained to better than one power of ten. For analogous calculations in terms of potential energy maps compare (103).

Photoelectric Kinetics

The electrochemical analogue of photochemistry has been little examined, although it promises to provide an important tool in the study of the mechanism of electrode processes (110).

It is possible to develop the theory of the equilibrium photopotential for an electrode in a solution of its ions by assuming that the only effect of the incident protons is to cause electron emission, thus leading to a change in the relative rates of the cathodic and anodic partial reactions maintaining the equilibrium $M^{z+}+ze_0 \rightleftarrows M$, and hence to a change of equilibrium potential, $\Delta\phi_p$. It is found (20) that the photopotential is linear with the logarithm of the intensity of the incident radiation if $\Delta\phi_p$ is $> RT/zF$ (cf. the Tafel equation) and linear with intensity at low values of intensity. $\Delta\phi_p$ is independent of concentration in dilute solutions, exhibits a threshold frequency and passes through a maximum with frequency, as has been observed (104).

Experimental work has also been carried out with electrodes covered with oxides in contact with solutions containing salts of the electrode material (105). The theory here concerns a barrier layer of nonstoichiometric oxide caused by a layer of stoichiometric oxide (106) and is analogous to that for photochemical effects on solid Cu/CuO.

Photoeffects are also complicated by the presence of organic substances (108) or redox equilibria (109), where photochemical effects may disturb the equilibrium and thus give photopotentials as secondary effects.

The electro-evolution of H_2 and O_2 was found by Hillson & Rideal (110) to be accelerated by light of 4000 to 2000 Å. These workers concluded that the r. d. s. occurred after discharge and that in the steady-state electrodes were covered with H. Although none of the systems examined have been investigated with regard to both b and ν, this conclusion seems out of accord with other evidence on the h. e. r., particularly at metals of lower i_0 values.

[13] Namely, (20), that $\beta = \mathrm{Tan}\,\phi/(\mathrm{Tan}\,\theta + \mathrm{Tan}\,\phi)$ where θ and ϕ are the angles made with the horizontal by the potential-energy-distance relations for the complexes $H^+ - H_2O$ and $H - M$, respectively.

Sonic Electrode Kinetics

When sound waves impinge upon a gas electrode, an a. c. potential of ca. 10 mv. for a pressure amplitude of one atm. results. The effect is independent of the electrode material (112, 113). Passage of sound waves through a liquid imparts large periodic accelerations to the medium and these cause temperature and pressure variations to be set up. At sufficiently low concentration, the electrode responds reversibly and the thermodynamic theory of such effects has been given by Yeager & Hovorka (114).

At ultrasonic frequencies the electrode behaves irreversibly and secondary effects occur, e.g., the ohmic overpotential in the vicinity of the electrode varies as a result of the periodic change in bubble size produced by the ultrasonic waves (115).

The rate of the h. e. r. in aqueous acid solutions is increased some five to ten times when a Pt electrode is irradiated with sound waves of intensity 1 watt $cm.^{-2}$ and $\nu = 300$ kc. sec^{-1}. The symmetry factor for the reaction remains unchanged. On cessation of the irradiation, the reaction rate is roughly halved but is not reduced to its original velocity before irradiation until some minutes after the current is switched off (116). It seems improbable that changes in gas pressure affect the reaction rate, which has been found to be independent of gas pressure at Hg (29) and Ni (7) electrodes. It is more likely that cavitation causes the removal of impurities adsorbed on the electrode surface and thus leads to an increase in reaction rate (116). The fact that the velocity does not decrease to its original value on termination of radiation probably means that impurities do not completely readsorb whilst H_2 is being evolved.

Ultrasonic irradiation increases the velocity of metal deposition in diffusion controlled reactions (117). This is due to the increase in limiting current caused by a smoothing out of the concentration gradient at the metal-solution interface, as has been proved by the use of Schlieren photographs (118). Characteristics of metal deposition can also be modified (119). Acceleration of the rate of hydrogen evolution corrosion is brought about by irradiation (113), as would be expected from the effects on the h. e. r. discussed.

Separation of Isotopes

A new electrochemical method for the separation of isotopes depends on the different mobilities of the isotopic ions; if an electrolytic solution is streamed counter to the motion of the isotopic ions at a rate such that the slower isotope is reduced to zero velocity with respect to the tube through which the electrolytic solution is streamed, a greater amount of the faster moving isotope reaches the cathode (120). The older method of separation depends on differences in the rate of the electrodeposition reactions of the isotopic ions. Few recent experimental results [see ref. (20)] in this field have been published.

Discussions of the theory of the separation of H and D have involved one or more of the following assumptions: (*i*) The slow stage in the electroevolution of H_2 at Hg differs from (A); (*ii*) The different activities of the H and D ions in solution could be neglected; (*iii*) Only the differences in the zero point energies of H and D-containing compounds affected the rate of their evolution; (*iv*) The heat of activation, not its free energy, primarily controls the reaction rate. It is now possible to apply more recent work on the calculation of the free energy of activation of proton discharge to a theoretical evaluation of the separation factor (20). The proportion of HOD and D_2O in ordinary water can be calculated from known equilibrium constants and from this and the differences of the interaction energies of D_2O-D, HOD-D and H_2O-D compared with that of H_2O-H, the concentrations of the various ions present can be approximately obtained. It is found that the only important entities for discharge are H_3O^+ and $HOHD^+$. Knowledge for the H and D-containing systems of the ionization energies of the atoms, the heats of hydration of the ions, their zero point energies, and the heat of dissociation of the molecules, allows the difference in the heat of activation for proton and deuteron transfer to be calculated. A rough estimate of the difference in entropy of activation can also be made. The numerical result of 2 for the separation factor compares reasonably with the value of 3–4 experimentally determined for Hg.

Polyelectrodes

If no net current passes through a polyelectrode, its steady-state mixed potential can be calculated, e.g., in metal dissolution, by equating the forward current for the evolution of H_2 to the anodic current for the dissolution of the metal (20). The rate of the latter may be activation or diffusion controlled. Thus, the mixed potential of the dissolving metal may be evaluated, and the resultant expression shows that, assuming that the exchange current for the metal dissolution is much greater than $(i_0)_H$, the mixed potential during dissolution is close to that of the reversible value for the metal in a solution of its ions. The dependence of the mixed potential on pH is shown to be diagnostic of diffusion and activation control for the metal dissolution.

The rate of dissolution of an isolated metal can be obtained by substituting the expressions for the mixed potential into the steady-state equation for the rate of dissolution or hydrogen evolution. The resulting expression shows that dissolution commences when

$$\Delta\phi_{R,H} > \Delta\phi_{R,M}, \qquad 56.$$

where R represents reversible, in agreement with simple thermodynamic considerations. If the pH is only slightly below that corresponding to (56), the rate of dissolution depends little on a_{H^+}. At higher values of a_{H^+} the rate of dissolution is proportional to $a_{H^+}^{1/2}$ and in concentrated acid solutions to a_{H^+} (20).

Dissolution of metals in acids having reducible groups, or not involving

the evolution of H_2, can be treated similarly if the mechanism for the removal of electrons which replaces proton discharge is known. Thus, the rate of dissolution of Cu is proportional to the concentration of HNO_3 molecules (121), because in the reduction of HNO_3 at a metal surface, electrons are removed by NO_2 groups and the rate of production of these depends on the electroreduction of HNO_3 (cf. equations 51, 52, 53).

A graphical method of evaluating the mixed potential of a complex polyelectrode system containing any number of metals is due to Tomashov (122). The mixed potential is found by plotting a series of $\eta - i$ relations for the cathodic and anodic polarizations at each electrode material composing the polyelectrode. The net curves for cathodic and anodic polarization can be drawn by adding all the currents for the cathodic currents and analogously for the anodic currents. The point of intersection of the net cathodic and anodic current gives the mixed potential. Then, reference of the potential of any microelectrode in the macroelectrode, at a given c. d., to the mixed potential, indicates whether the microelectrode would be stable (cathodic) or unstable (anodic). The cathodic and anodic partial currents, and hence the rate of corrosion, can be evaluated. A similar method (123) is available for the determination of the stability of the elements in a system in which the local currents are controlled by the solution resistance.

Pourbaix (124) has used eq. 56 in drawing diagrams of the limiting potential at which dissolution commences against pH and thus greatly facilitating the estimation of the limiting pH for metal dissolution. The method indicates when corrosion will not occur, but allows no estimate of its rate.

Technique

Solution purification.—Reproducible measurements in electrode kinetics have, until recently been made difficult by irregularities in the Tafel lines and by time variation of overpotential at a given c. d. (particularly on solid electrodes). For the h. e. r. these difficulties can be eliminated if solutions are first subject to pre-electrolysis on an auxiliary cathode (38). Systematic studies of trace impurity affects on other electrode reactions are lacking although a similar sensitivity has been indicated for redox reactions (55). The validity of measurements for other reactions must remain in doubt unless the effect of intensive pre-electrolytic purification has been studied. Further. adsorption of organic substances is known to occur rapidly in comparison, for example, with diffusion processes (55), so that polarographic measurements of activation kinetics in solutions containing, e.g., gelatin may provide results on poisoned surfaces.

Cathodic pre-electrolysis reduces depolarizers, e.g., O_2, removes foreign cations by deposition; and leads to the adsorption of capillary-active impurities. Simple diffusion theory shows (76) that the efficacy of the first two processes is increased by high c. d., time and agitation. To reduce the concentration of a trace impurity by 10^4 times, the minimum period for pre-electrol-

ysis (at a c. d. close to i_L for the impurity concerned) is about 24 hr. In practice, somewhat greater times are used. The criterion of sufficient pre-electrolysis must be that continued purification no longer alters the kinetics in that solution.

It is sometimes also desirable to have present in the solution a sheet of highly adsorbing material, e.g., platinized Pt, to adsorb nonelectrolytic poisons.

Electrodes.—A satisfactory method for preparing the surface of a solid electrode in a reproducible state is to heat the electrode in a stream of H_2 to remove oxides, organic materials, etc., and seal it into a thin (As-free) glass bulb containing H_2. The bulb is introduced into the solution and, after pre-electrolysis, broken with a probe (125). Electrodes with stable films may require flashing (47).

In metal deposition, vacuum melting and single crystals have been used (126, 127), but hitherto not in highly purified solutions so that the value of the technique cannot be fully assessed.

Cells.—These are best constructed of As-free glass. Taps are accurately ground and able to withstand a light vacuum when moistened with the solvent used in the cell. To make full use of a purified solution it is desirable to have several electrodes in the same cell and this can be achieved by the use of sliding fit ground glass sleeves in which electrodes can be raised and lowered from the solution (125, 125a).

The construction of cells would be facilitated if it were possible to use a plastic (128), but the danger of contamination arises (129). A poisoning effect has been established with telcothene (130). Tephlon is said to give satisfactory results for the h. e. r. on Pt (131).

The problem of the optimum form of Luggin capillary does not appear to have been solved for all types of reactions. The difficulties arising are (*i*) the ohmic overpotential between the end of the capillary and electrode; and (*ii*) the possible screening effect of the capillary on the current lines near the electrode. Difficulty (*i*) can be diminished by making measurements at various distances from the electrode and extrapolating to zero distance, or by using a commutator. The dominant component of the ohmic overpotential is the potential difference across the diffusion layer which becomes very large when the current approaches the limiting current for the depositing entity [in the absence of excess indifferent electrolyte (20)].

That the Luggin capillary exerts no screening effect on overpotential measurements in H_2 evolution has been established by (*i*) agreement of the parameters of the Tafel equation for the h. e. r. between the results of independant work. This is the best agreement yet known in electrode kinetics (132), but was obtained without standardization of the capillary position; (*ii*) by the applicability of the Tafel equation over a range of c. d.'s of about 10^{11} amp. cm.$^{-2}$ (24). (The magnitude of the screening error would vary with c. d.); (*iii*) by specific tests of screening in which identical Tafel lines have

been established with the capillary at various distances from the electrode (76). In metal deposition kinetics, a screening effect has been claimed and a capillary pressed on the electrode with a hole in its side, near to the end, gives improved results (126). It is possible that the smaller potential difference between metal and solution which exists during metal deposition compared to that for H_2 evolution allows a greater local variation of potential over the surface to exist with metal deposition than with gas evolution.

Circuits.—Some developments (134) of the electronic commutator originated by Hickling (133) have been made. In one, (135) a gated bridge null detector is used in conjunction with a potentiometer and decay times of $5 \cdot 10^{-6}$ sec.$^{-1}$ have been used. Criticism of the electronic commutator has been refuted by direct comparison of results on the same cell with those obtained by a direct method (136).

Several developments of the potentiostat (138) also originated by Hickling (137), have been used in controlled potential electrolysis.

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[14] For example, cf. results in references (29) and (132), and also reference (23).

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